Simulation moléculaire : Problèmes dynamiques et hors d'équilibre

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"Wenn jemand sucht," sagte Siddhartha, "dann geschieht es leicht, daß sein Auge nur noch das Ding sieht, das er sucht, daß er nichts zu finden, nichts in sich einzulassen vermag, weil er nur immer an das Gesuchte denkt, weil er ein Ziel hat, weil er vom Ziel besessen ist. Suchen heißt: ein Ziel haben. Finden aber heißt: frei sein, offen stehen, kein Ziel haben."

"When someone is searching," said Siddhartha, "then it might easily happen that the only thing his eyes still see is that what he searches for, that he is unable to find anything, to let anything enter his mind, because he always thinks of nothing but the object of his search, because he has a goal, because he is obsessed by the goal. Searching means: having a goal. But finding means: being free, being open, having no goal."

Hermann Hesse, *Siddhartha*

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[1] Et encore toutes mes excuses à Cécile, qui, semblerait-il, a moins apprécié le week-end de relecture...

Contents

Part I

Introduction

1

General presentation of the results

Molecular simulation aims at understanding and predicting the macroscopic properties of matter from models at the microscopic scale. My scientific activity in this broad field can be decomposed depending on the physical framework: classical statistical physics on the one hand, and quantum physics on the other.

- My works in statistical physics can further be classified into two categories: the computation of equilibrium properties (Section 1.1) and the study of nonequilibrium systems (Section 1.2). In both cases, these studies are often performed with nonequilibrium or nonlinear dynamics, the distinction arising from the fact that the stationary state of the dynamics is either an equilibrium one (possibly upon an appropriate correction) or a nonequilibrium one.
- Section 1.3 presents some results for time dependent dynamics in quantum physics.

Publications from works done or substantially initiated during my PhD are referred to as [Pxx], while the subsequent contributions are listed as [Hxx] (see the bibliography in Section 1.4).

1.1 (Non)Equilibrium methods to compute equilibrium properties

The theoretical and numerical analysis of some nonequilibrium dynamics to compute efficiently equilibrium properties is presented Chapter 2. This research path was initiated during my PhD work [P8], with an emphasis on free energy computations [P2, P6, P9, P10, P12]

With M. Rousset and T. Lelièvre, we wrote a book summarizing our current understanding of the available techniques to compute free energy differences [B1]. In the past years, I studied in particular equilibrium or nonequilibrium constrained Langevin dynamics [H29] and nonlinear techniques where the free energy is updated depending on the current state of the system [H21]. I also considered an application of free energy methods to Bayesian statistics, where there is no physical intuition about the choice of the parameter indexing the transition [H27]; and in condensed matter physics to discuss the isentropic character of release waves [H17].

Motivated by a concrete application, namely the computation of Hugoniot curves (a question asked by my colleagues at CEA-DAM), I also proposed a method to sample configurations satisfying a constraint in average [H15]. This method was then successfully applied for computations of properties of real materials in [H23].

1.2 Nonequilibrium systems and transport properties

Chapter 3 is devoted to nonequilibrium systems in a steady state. During my PhD, I proposed reduced models to compute shock and detonation waves [P1, P5, P11]. Recently, this model was applied to systems more realistic than the ones I studied [H25].

In the past years, I turned to the numerical computation of transport properties (thermal conductivity, shear viscosity, ...), with an emphasis on nonequilibrium molecular dynamics techniques. This research path was initiated during my post-doctoral work at IMPMC. Most of my contributions in this field focus on the thermal conductivity of one dimensional systems, perturbed in various ways: stochastic noises preserving some invariants of the system [H22, H28], atoms with random masses [H16, H18], mechanical forcings applied at the boundary of the system [H24]. In the framework of the PhD work of R. Joubaud, I also studied the computation of the shear viscosity [H26].

1.3 Time-dependent problems in quantum physics

The common denominator in the contributions summarized in Chapter 4 are the time dependence of the quantum models I have considered. The part of my PhD work concerned with quantum theory was focused on methods for finding the ground-state of molecular systems in quantum chemistry [P3, P4, P7, P13]. My interests shifted towards models of quantum physics during my post-doctoral work at IMPMC.

In a series of papers with Ch. Brouder and G. Panati, we studied the Gell-Mann and Low technique, which provides a way to compute eigenstates of a perturbed Hamiltonian $H_0 + V$ from eigenstates of the reference Hamiltonian H_0, using some fictitious dynamics in the adiabatic limit. Our mathematical result extends previous studies to the case when the eigenspace of the reference Hamiltonian is degenerate [H20]. This result was motivated by the simple analytical example described in [H14]. We also presented some physical implications in [H19].

Very recently, we studied with E. Cancès the behavior of defects in crystals under an external, time dependent forcing [H30]. The aim of this study was to extend previous results on the static (time-independent) response of crystals to the case of time-dependent forcings. There is therefore a genuine time dependence in this model, which allows to derive, in some spatial homogenization limit, the expression of the frequency-dependent permittivity of a crystal in terms of its band structure.

1.4 Publications

I list here my publications by types, decomposing the publications in peer-reviewed journals into two categories, depending on whether the material has been produced or substantially initiated during my PhD, or afterwards.

Publications from works completed or initiated during my PhD

[P1] G. Stoltz, Shock waves in an augmented one-dimensional chain, *Nonlinearity* **18** (2005) 1967-1985

[P2] M. Rousset and G. Stoltz, An interacting particle system approach for molecular dynamics, *J. Stat. Phys.* **123**(6) (2006) 1251-1272

[P3] E. Cancès, M. Lewin and G. Stoltz, The electronic ground state energy problem: a new reduced density matrix approach, *J. Chem. Phys.* **125** (2006) 064101

[P4] A. Scemama, T. Lelièvre, G. Stoltz, E. Cancès and M. Caffarel, An efficient sampling algorithm for Variational Monte Carlo, *J. Chem. Phys.* **125** (2006) 114105

[P5] G. Stoltz, A reduced model for shock and detonation waves. I. The inert case, *Europhys. Lett.* **76**(5) (2006) 849-855

[P6] T. Lelièvre, M. Rousset and G. Stoltz, Computation of free energy differences through nonequilibrium stochastic dynamics: the reaction coordinate case, *J. Comput. Phys.* **222**(2) (2007) 624-643

[P7] A.F. Izmaylov, V.N. Staroverov, G. Scuseria, E.R. Davidson, G. Stoltz and E. Cancès, The effective local potential method: Implementation for molecules and relation to approximate optimized effective potential techniques, *J. Chem. Phys.* **126** (2007) 084107

[P8] E. Cancès, F. Legoll and G. Stoltz, Theoretical and numerical comparison of some sampling methods, *ESAIM-Math. Model. Num.* **41**(2) (2007) 351-390

[P9] G. Stoltz, Path sampling with stochastic dynamics: some new algorithms, *J. Comput. Phys.* **225** (2007) 491-508

[P10] T. Lelièvre, M. Rousset and G. Stoltz, Computation of free energy profiles with parallel adaptive dynamics, *J. Chem. Phys.* **126** (2007) 134111

[P11] J.-B. Maillet, L. Soulard et G. Stoltz, A reduced model for shock and detonation waves. II. The reactive case, *Europhys. Lett.* **78**(6) (2007) 68001

[P12] T. Lelièvre, M. Rousset and G. Stoltz, Long-time convergence of an adaptive biasing force method, *Nonlinearity* **21** (2008) 1155-1181

[P13] E. Cancès, G. Stoltz, G. Scuseria, V. Staroverov and E. Davidson, Local exchange potentials for electronic structure calculations, *MathS In Action* **2** (2009) 1-42

Publications from works initiated after the PhD defense

[H14] Ch. Brouder, G. Stoltz and G. Panati, Adiabatic approximation, Gell-Mann and Low theorem and degeneracies: A pedagogical example, *Phys. Rev. A* **72** (2008) 042102

[H15] J.B. Maillet and G. Stoltz, Sampling constraints in average: The example of Hugoniot curves, *Appl. Math. Res. Express* **2008** abn004 (2009)

[H16] G. Stoltz, M. Lazzeri and F. Mauri, Thermal transport in isotopically disordered carbon nanotubes, *J. Phys.:Cond. Matter* **21** (2009) 245302

[H17] J.-B. Maillet, E. Bourasseau, L. Soulard, J. Clerouin and G. Stoltz, Constant entropy sampling and release waves of shock compressions, *Phys. Rev. E* **80** (2009) 021135

[H18] G. Stoltz, N. Mingo and F. Mauri, Reducing the thermal conductivity of carbon nanotubes below the random isotope limit, *Phys. Rev. B* **80** (2009) 113408

[H19] Ch. Brouder, G. Panati and G. Stoltz, Many-body Green function of degenerate systems, *Phys. Rev. Lett.* **103** (2009) 230401

[H20] Ch. Brouder, G. Panati and G. Stoltz, Gell-Mann and Low formula for degenerate unperturbed states, *Ann. I. H. Poincare-Phy.* **10**(7) (2010) 1285-1309

[H21] B. M. Dickson, F. Legoll, T. Lelièvre, G. Stoltz and P. Fleurat-Lessard, Free energy calculations: An efficient adaptive biasing potential method, *J. Phys. Chem. B* **114**(17) (2010) 5823-5830

[H22] A. Iacobucci, F. Legoll, S. Olla and G. Stoltz, Thermal conductivity of the Toda lattice with conservative noise, *J. Stat. Phys.* **140**(2) (2010) 336-348

[H23] E. Bourasseau, J.-B. Maillet, N. Desbiens and G. Stoltz, Microscopic calculations of Hugoniot curves of neat TATB and of its detonation products, *J. Phys. Chem. A* **115** (39) (2011) 10729-10737

[H24] A. Iacobucci, F. Legoll, S. Olla and G. Stoltz, Negative thermal conductivity of chains of rotors with mechanical forcing, *Phys. Rev. E* **84** (2011) 061108

[H25] J.-B. Maillet, G. Vallverdu, N. Desbiens and G. Stoltz, Molecular simulations of shock to detonation transition in nitromethane, *Europhys. Lett.* **96** (2011) 68007

[H26] R. Joubaud and G. Stoltz, Nonequilibrium shear viscosity computations with Langevin dynamics, *Multiscale Model. Sim.* **10** (2011) 191-216

[H27] N. Chopin, T. Lelièvre and G. Stoltz, Free energy methods for efficient exploration of mixture posterior densities, *Stat. Comput.* **22**(4) (2012) 897-916

[H28] C. Bernardin and G. Stoltz, Anomalous diffusion for a class of systems with two conserved quantities, *Nonlinearity* **25** (2012) 1099- 1133

[H29] T. Lelièvre, M. Rousset and G. Stoltz, Langevin dynamics with constraints and computation of free energy differences, to appear in *Math. Comput.* (2012)

[H30] E. Cancès and G. Stoltz, A mathematical formulation of the random phase approximation for crystals, accepted in *Ann. I. H. Poincare-An.* (2012)

Submitted works

[S1] M. Dobson, F. Legoll, T. Lelièvre and G. Stoltz, Derivation of Langevin ynamics in a non-zero background flow, *HAL preprint* **00680278** (2012)

Book

[B1] T. Lelièvre, M. Rousset and G. Stoltz, Free Energy Computations: A Mathematical Perspective (Imperial College Press, 2010)

Conference proceedings and general audience articles

[C1] B. Leimkuhler and G. Stoltz, Sampling techniques for computational statistical physics, in *Encyclopedia of Applied and Computational Mathematics*, B. Engquist (Ed.) (Springer, 2012)

[C2] G. Stoltz, Calculation of ensemble averages, in *Encyclopedia of Applied and Computational Mathematics*, B. Engquist (Ed.) (Springer, 2012)

[C3] G. Stoltz, Computation of free energy differences, in *Encyclopedia of Applied and Computational Mathematics*, B. Engquist (Ed.) (Springer, 2012)

[C4] E. Cancès, M. Lewin and G. Stoltz, The microscopic origin of the macroscopic dielectric permittivity of crystals: A mathematical viewpoint, in *Numerical Analysis of Multiscale Computations*, B. Engquist, O. Runborg, Y.-H. R. Tsai. (Eds.), Lecture Notes in Computational Science and Engineering, Vol. 82 (Springer, 2011) 87 - 125

[C5] F. Legoll, T. Lelièvre and G. Stoltz, Some remarks on sampling methods in Molecular Dynamics, Proceedings of CANUM 2006, *ESAIM Proc* **22** (2008) 217-233

Part II

Presentation of some results

2

(Non)Equilibrium methods to compute equilibrium properties

This chapter starts in Section 2.1 with a brief presentation of computational statistical physics. One important aim in molecular simulation is the computation of average properties at fixed thermodynamic conditions, see (2.2) below. However, not all properties of interest can be written as averages with respect to a thermodynamic measure with given thermodynamic conditions. A very important example is the computation of the free energy, which is considered in Section 2.2 (based on [P2, P6, P9, P10, P12, H17, H21, H27, H29, B1]). Another situation which does not fall within the standard framework of statistical physics is the case when the thermodynamic conditions are not fixed a priori, but are part of the problem. This is the case when the system should satisfy a constraint in average, the thermodynamic conditions being precisely such that this constraint is indeed satisfied. An approach to this problem is described in Section 2.3 (based on [H15, H23]).

2.1 Computational statistical physics

Statistical physics provides a way to obtain macroscopic quantities starting from systems described at the microscopic level. In this framework, the state of the system is described by some probability measure, the precise choice of the measure depending on the invariant quantities considered

(number of particles or chemical potential, volume or pressure, energy or temperature). We focus in this chapter on the canonical measure, which is the equilibrium probability distribution describing microscopic states of a system at fixed temperature (fixed average energy). Many theoretical concepts and numerical techniques presented in this chapter can however straightforwardly be extended to other thermodynamic ensembles, or even to general (non-physical) probability measures such as the ones encountered in Bayesian Statistics.

The configuration of a classical N-body system is denoted by $(q,p) \in \mathcal{E}$. Typically, in dimension $d=3$, $\mathcal{E} = \mathcal{M} \times \mathbb{R}^{3N}$ with $\mathcal{M} = \mathbb{R}^{3N}$ when the system is confined by an external potential, or $\mathcal{M} = \mathcal{D}^N$ when the system is enclosed in a periodic simulation box $\mathcal{D} = (L\mathbb{T})^3$ (with $\mathbb{T} = \mathbb{R}\backslash\mathbb{Z}$). We assume for simplicity that the system is described by a separable Hamiltonian

$$H(q,p) = \frac{1}{2} p^T M^{-1} p + V(q),$$

where the interaction potential V is a smooth function, and the mass matrix is a constant, positive definite, symmetric matrix M (typically a diagonal matrix $M = \mathrm{Diag}(m_1 \mathrm{Id}_3, \cdots, m_N \mathrm{Id}_3) \in \mathbb{R}^{3N \times 3N}$ with $m_i > 0$ for all $i = 1, \ldots, N$). Generalizations to non-separable Hamiltonians are possible. The canonical measure reads

$$\mu(dq\,dp) = Z^{-1}\, \mathrm{e}^{-\beta H(q,p)}\, dq\, dp, \qquad Z = \int_{\mathcal{E}} \mathrm{e}^{-\beta H}, \tag{2.1}$$

where Z is the normalizing constant ensuring that μ is indeed a probability distribution (we assume $Z < +\infty$), and $\beta = (k_{\mathrm{B}} T)^{-1}$ (with k_{B} the Boltzmann constant) is proportional to the inverse temperature. Macroscopic quantities $\mathscr{A}$, such as the pressure for instance, are obtained by averaging observables, which are functions of the microscopic state, with respect to the probability measure describing the macroscopic state of the system:

$$\mathscr{A} = \int_{\mathcal{E}} A(q,p)\, \mu(dq\,dp). \tag{2.2}$$

The actual issue is the sampling of the configurational part of the canonical measure since momenta follow a Gaussian distribution. The high dimensional integral (2.2) cannot be computed using standard quadrature methods. It is approximated in practice by ergodic averages of appropriate dynamics:

$$\mathscr{A} = \lim_{T \to +\infty} \frac{1}{T} \int_0^T A(q_t, p_t)\, dt. \tag{2.3}$$

2.1.1 Sampling the canonical measure

Let us now present some well-known stochastic dynamics satisfying (2.3). An important requirement is that these dynamics should admit the canonical measure as invariant measure, which is the case when the canonical measure is a stationary solution of the Fokker-Planck equation. For a general stochastic dynamics (in the Itô sense)

$$dx_t = b(x_t)\, dt + \sigma(x_t)\, dW_t, \tag{2.4}$$

where $x_t \in \mathbb{R}^n$, W_t is a standard n-dimensional Brownian motion, and b and σ are smooth functions, the Fokker-Planck equation reads

$$\partial_t \psi = \mathcal{A}^* \psi, \tag{2.5}$$

where $\psi(t,x)$ is the law at time t of x_t, and $\mathcal{A}^*$ is the adjoint (on $L^2(\mathbb{R}^n)$) of the generator

$$\mathcal{A} = b \cdot \nabla + \frac{1}{2}\sigma\sigma^T : \nabla^2 = b \cdot \nabla + \frac{1}{2}\sum_{i,j=1}^{n} \left(\sigma\sigma^T\right)_{i,j} \partial_{x_i}\partial_{x_j}. \tag{2.6}$$

One dynamics admitting the canonical measure (2.1) as invariant measure is the Langevin dynamics:

$$\begin{cases} dq_t = M^{-1}p_t\,dt, \\ dp_t = -\nabla V(q_t)\,dt - \gamma(q_t)M^{-1}p_t\,dt + \sigma(q_t)\,dW_t, \end{cases} \tag{2.7}$$

where W_t is a standard $3N$-dimensional Brownian motion, and $\gamma(q), \sigma(q)$ are $3N \times 3N$ position dependent real matrices satisfying the fluctuation-dissipation identity

$$\sigma(q)\,\sigma^T(q) = \frac{2}{\beta}\gamma(q). \tag{2.8}$$

The Langevin dynamics may be seen as some modification of the Hamiltonian dynamics with two added components: a damping term $-\gamma(q_t)M^{-1}p_t\,dt$ (dissipation) and a random forcing term $\sigma(q_t)\,dW_t$ (fluctuation). The energy dissipation due to damping is compensated by the random forcing in such a way that the temperature of the system remains $T = (k_B\beta)^{-1}$. Under suitable assumptions on the potential V, the friction and the dissipation matrices, the dynamics (2.7) can be proved to be ergodic and (2.3) holds (see for instance the discussion in [P8]). Another important dynamics is the overdamped Langevin dynamics, which is ergodic for the marginal of the canonical measure in the position variables:

$$dq_t = -\nabla V(q_t)\,dt + \sqrt{\frac{2}{\beta}}\,dW_t. \tag{2.9}$$

This dynamics can be obtained as a limit of the Langevin dynamics (2.7), either when the friction goes to infinity (with an appropriate time rescaling) or for vanishing masses; see [B1, Section 2.2.4] for further precisions.

2.1.2 Beyond the computation of standard average properties

The methods presented in this chapter can be used to compute equilibrium properties different from the standard average properties (2.2).

- Free energy differences are important quantities to describe the relative likelihoods of states of a system. Section 2.2 presents various new techniques to compute free energy differences.
- In some instances, it is desirable to consider ensembles such that some constraint is satisfied on average. In this setting, the extensive or intensive parameters indexing the state of the system (such as the temperature or the volume in the canonical ensemble) may be seen as unknowns whose value has to be fixed. Section 2.3 summarizes my work in this direction, which was triggered by numerical concerns of physicists at CEA/DAM.

Many methods described in this chapter turn out to be based on nonequilibrium or nonlinear dynamics, although their stationary state is either an equilibrium one, or can be mapped back to an equilibrium one by an appropriate correction. The nonequilibrium dynamics considered in this chapter (see Section 2.2.3) are in fact time-inhomogeneous stochastic evolutions occuring over finite times. They are termed "nonequilibrium" since the law of the process at time t is not a canonical distribution. They should be distinguished from nonequilibrium dynamics in their steady states which are studied in Chapter 3.

2.2 Free energy computations

This section starts with an overview of techniques to compute free energy differences (see Section 2.2.1). One of our contributions is then highlighted: the computation of free energy differences indexed by a geometric parameter (the so-called reaction coordinate, defined in Section 2.2.1.1), when the underlying dynamics is of Langevin type [H29]. Two methods are considered: thermodynamic integration (Section 2.2.2) and nonequilibrium dynamics (Section 2.2.3).

2.2.1 A general overview

Free energy is a central concept in thermodynamics and in modern studies on biochemical and physical systems. Typical examples studied by computer simulations include the solvation free energies (which is the free energy difference between a molecule *in vacuo* and the same molecule surrounded by solvent molecules) and the binding free energy of two molecules (which determines whether a new drug can have an efficient action on a given protein).

The statistical physics definition of the free energy in the canonical ensemble (2.1) as the logarithm of the partition function

$$F = -\frac{1}{\beta} \ln \int_{\mathcal{E}} \mathrm{e}^{-\beta H(q,p)} \, dq \, dp \tag{2.10}$$

can be motivated by an analogy with macroscopic thermodynamics, where

$$F = U - TS, \tag{2.11}$$

U being the internal energy of the system, and S its entropy. The microscopic definition of the internal energy is the average energy as given by the laws of statistical physics:

$$\mathbb{E}_\mu(H) = Z^{-1} \int_{\mathcal{E}} H(q,p) \, \mathrm{e}^{-\beta H(q,p)} \, dq \, dp, \tag{2.12}$$

while the microscopic counterpart of the thermodynamic entropy is the statistical entropy (see [11])

$$\mathfrak{S} = -k_\mathrm{B} \int_{\mathcal{E}} \ln \left(\frac{d\mu}{dq \, dp} \right) \, d\mu. \tag{2.13}$$

Replacing U and S in (2.11) by (2.12) and (2.13) respectively, we obtain the definition (2.10).

2.2.1.1 Free energy differences

In many applications, the important quantity is actually the free energy difference between two macroscopic states of the system, rather than the free energy itself (see [30]). Free energy differences allow to quantify the relative likelihood of different states. A state should be understood here as either

(i) the collection of all possible microscopic configurations distributed according to the canonical measure associated with a Hamiltonian H_λ depending on some parameter λ (called the alchemical parameter). The parameter λ is then the index of the state, and the free energy difference reads

$$F(1) - F(0) = -\beta^{-1} \ln \left(\frac{\displaystyle\int_{\mathcal{E}} \mathrm{e}^{-\beta H_1(q,p)} \, dq \, dp}{\displaystyle\int_{\mathcal{E}} \mathrm{e}^{-\beta H_0(q,p)} \, dq \, dp} \right). \tag{2.14}$$

Typically, λ is a parameter of the potential energy function, or the intensity of an external perturbation (such as a magnetic field for Ising systems);

(ii) the collection of all possible microscopic configurations of the phase-space $\mathcal{E} = \mathcal{M} \times \mathbb{R}^{3N}$, distributed according to the canonical measure (2.1), and satisfying a given macroscopic constraint $\xi(q) = z$, where $\xi : \mathcal{M} \to \mathbb{R}^m$ with m small. Such macroscopic constraints are for instance the values of a few dihedral angles in the carbon backbone of a protein, or the end-to-end distance of a long molecule. The function ξ is called the "reaction coordinate". In this case, the configurations are restricted to the set

$$\Sigma(z) = \Big\{ (q,p) \in \mathcal{E} \,\Big|\, \xi(q) = z \Big\} \tag{2.15}$$

where z is the index of the state, and the free energy difference to compute reads

$$F(1) - F(0) = -\beta^{-1} \ln \left(\frac{\displaystyle\int_{\Sigma(1)\times\mathbb{R}^{3N}} \mathrm{e}^{-\beta H(q,p)}\, \delta_{\xi(q)-1}(dq)\, dp}{\displaystyle\int_{\Sigma(0)\times\mathbb{R}^{3N}} \mathrm{e}^{-\beta H(q,p)}\, \delta_{\xi(q)}(dq)\, dp} \right). \tag{2.16}$$

A rigorous definition of the conditional measures $\delta_{\xi(q)-z}(dq)$ can be given using the co-area formula (see [4, 57] as well as [B1, Chapter 3]): for any test functions $f : \mathbb{R}^m \to \mathbb{R}$ and $g : \mathcal{M} \to \mathbb{R}$,

$$\int_{\mathcal{M}} f(\xi(q))\, g(q)\, dq = \int_{\mathbb{R}^m} f(z) \left(\int_{\Sigma(z)} g\, \delta_{\xi(q)-z}(dq) \right) dz.$$

The case of free energy differences indexed by a reaction coordinate is more technical than the case of free energy differences indexed by an alchemical parameter. One of our aims in the study of numerical techniques to compute free energy differences has precisely been the extension of several techniques proposed for alchemical transitions to the reaction coordinate case (see in particular [P6, H29]), or the mathematical study of techniques proposed in the reaction coordinate case (see [P10, P12]).

Free energy techniques can also be used in some contexts to compute entropy differences, and not free energy differences, using appropriate alchemical transformations. This is what we have done in [H17] to study the entropy increase when a hot and dense system, compressed in a box, is allowed to expand when one of the boundaries of the box is removed. This procedure models the behavior of materials after a shock compression.

2.2.1.2 Numerical methods to compute free energy differences

Together with Mathias Rousset and Tony Lelièvre, we wrote a review book on the numerical methods to compute free energy differences (see [B1]). Most of the currently available strategies fall within the following four classes, in order of increasing mathematical technicality:

(i) Methods of the first class are based on straightforward sampling methods. In the alchemical case, the free energy perturbation method, introduced in [159], recasts free energy differences as usual canonical averages. In the reaction coordinate case, usual sampling methods can also be employed, using histogram methods [138];

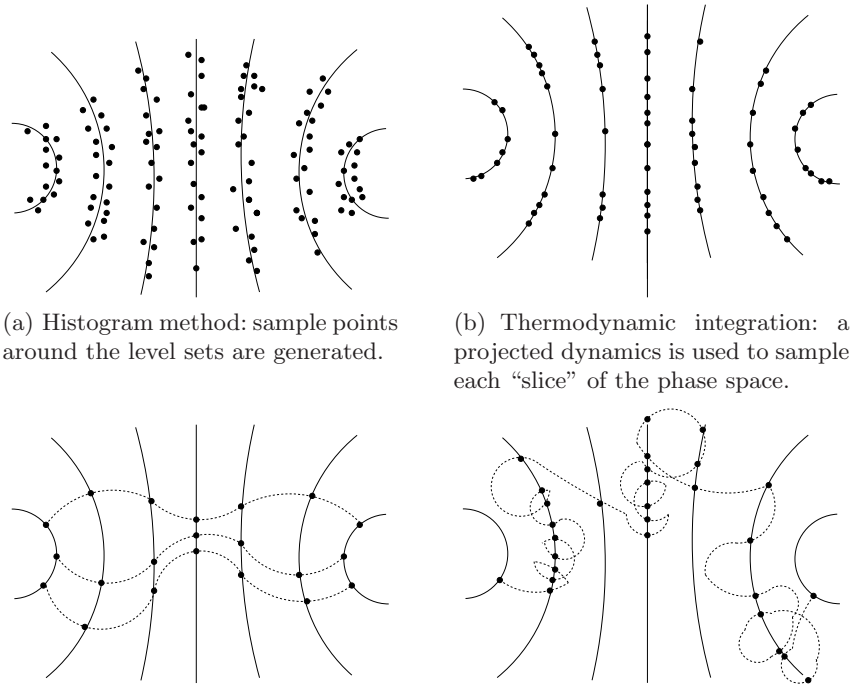
(ii) The second technique, dating back to [97], is thermodynamic integration, which mimics the quasi-static evolution of a system as a succession of equilibrium samplings (this amounts to considering an infinitely slow switching between the initial and final states). In this case, constrained equilibrium dynamics have to be considered. Section 2.2.2 presents the procedure when constrained Langevin dynamics are used.

(iii) A more recent class of methods is based upon dynamics with an imposed "schedule" for the reaction coordinate or the alchemical parameter: the system is started off at equilibrium, and then the value of the reaction coordinate $z(t)$ or of the alchemical parameter $\lambda(t)$ is varied

in time at a finite rate and in a predefined manner, independently of the state of the system. The system therefore does not remain at equilibrium. Equilibrium properties can however be recovered from the nonequilibrium trajectories with a suitable exponential reweighting, see [92, 93]. Section 2.2.3 presents a recent extension based on Langevin dynamics in the reaction coordinate case.

(iv) Finally, adaptive biasing dynamics may be used in the reaction coordinate case. The switching schedule is not imposed *a priori*, but a biasing term in the dynamics forces the transition by penalizing the regions which have already been visited (see Section 2.2.1.3 for further precisions).

We refer to Figure 2.1 for a schematic representation of the computational methods in the reaction coordinate case.



(a) Histogram method: sample points around the level sets are generated.

(b) Thermodynamic integration: a projected dynamics is used to sample each "slice" of the phase space.

(c) Nonequilibrium dynamics: the switching schedule is imposed *a priori* and is the same for all trajectories.

(d) Adaptive biasing dynamics: the system is forced to leave regions where the sampling is sufficient.

Fig. 2.1. Cartoon comparison of the different techniques to compute free energy differences in the reaction coordinate case.

2.2.1.3 Free energy based importance sampling

Beside physical motivations to compute free energy differences, a computational motivation is to overcome sampling barriers encountered when computing canonical averages (see the discussion in [B1, Section 1.3.3]). Indeed, it is often the case in practice that the trajectories generated by the numerical method remain trapped for a long time in some region of the phase space, and only occasionally hop to another region, where they also remain trapped – a behavior known as metastability. Chemical and physical intuition may guide the practitioners of the field toward the identification of some slowly evolving degree of freedom responsible for the metastable behavior of the system. This quantity is a function $\xi(q)$ of the configuration of the system, where $\xi : \mathcal{M} \to \mathbb{R}^m$

with m small. The framework to consider is therefore the case of transitions *indexed by a reaction coordinate*.

If the function ξ is well chosen (*i.e.* if the dynamics in the direction orthogonal to ξ is not too metastable, which we henceforth assume), the free energy can be used as a biasing potential to accelerate the sampling, relying on importance sampling strategies. More precisely, we sample the probability measure[1]

$$\widetilde{\mu}(dq\,dp) = \widetilde{Z}^{-1}\,\mathrm{e}^{-\beta[H(q,p)-F(\xi(q))]}\,dq\,dp, \qquad \widetilde{Z} = \int_{\mathcal{E}} \mathrm{e}^{-\beta(H-F\circ\xi)},$$

using for instance the *biased* Langevin dynamics

$$\left\{ \begin{array}{l} dq_t = M^{-1}p_t\,dt, \\ dp_t = \Big(-\nabla V(q_t) + F'(\xi(q))\nabla\xi(q)\Big)dt - \gamma M^{-1}p_t\,dt + \sqrt{\dfrac{2\gamma}{\beta}}\,dW_t. \end{array} \right. \tag{2.17}$$

Canonical averages (2.2) with respect to the original canonical measure (2.1) are then obtained by an appropriate reweighting of the trajectory of the biased dynamics as

$$\mathbb{E}_\mu(A) = \frac{\mathbb{E}_{\widetilde{\mu}}(A\,\mathrm{e}^{-\beta F\circ\xi})}{\mathbb{E}_{\widetilde{\mu}}(\mathrm{e}^{-\beta F\circ\xi})} = \lim_{T\to+\infty} \frac{\displaystyle\int_0^T A(q_t,p_t)\,\mathrm{e}^{-\beta F(\xi(q_t))}\,dt}{\displaystyle\int_0^T \mathrm{e}^{-\beta F(\xi(q_t))}\,dt}. \tag{2.18}$$

The terminology "reweighting" is motivated by the fact that all sampled configurations (q_t, p_t) do not have the same weight in the average over the trajectory.

This viewpoint allows to use free energy techniques in other fields than the one traditionally covered by statistical physics, such as Bayesian Statistics. In order to have an efficient method, the weights $\mathrm{e}^{-\beta F(\xi(q_t))}$ should not be too degenerate, that is, the average in (2.18) should not be dominated by a few values dominant values. We have shown in [H27] that free energy based importance sampling can be used in Bayesian statistics. More precisely, we have discussed various choices of reaction coordinates for a mixture model, and tested the efficiency of the associated importance sampling procedure.

Adpative importance sampling

Instead of first obtaining an estimate of the free energy profile, and then running a biased dynamics such as (2.17), it is possible to use adaptive importance sampling strategies where estimates of the free energy are computed on-the-fly. This is performed by integrating a dynamics biased by an approximation F_t of the free energy, and updating this approximation in such a way that F_t converges to the free energy F in the longtime limit. Many techniques have been proposed in the literature. They can be classified into two categories (see the classification we have proposed in [P10]):

(i) methods in which the free energy itself is updated, such as the Wang-Landau dynamics [151, 152], the nonequilibrium metadynamics [90], or self-healing umbrella sampling [112].
(ii) methods in which the gradient of the free energy is updated (such as the Adaptive Biasing Force [37]).

We refer to [B1, Section 5.1] for a precise description of the above mentioned dynamics and a general presentation of adaptive importance sampling techniques for free energy computations. Our

[1] In fact, in order to ensure that the normalization constant $\widetilde{Z}$ is finite when the state-space is not compact, it may be necessary to truncate the free energy and consider the biasing potential $F(\xi)\mathbf{1}_{a\leqslant\xi\leqslant b}$ for well chosen values $-\infty < a \leqslant b < +\infty$; or, rather, some smooth approximation of this potential.

contributions to this domain involve the mathematical study of the convergence of the adaptive biasing force method using entropy estimates (see [P12]), and some extension of the self-healing umbrella technique (see [H21]).

2.2.2 Thermodynamic integration

The basic ideas behind thermodynamic integration are presented in the simple setting of alchemical transitions in Section 2.2.2.1. The extension to transitions indexed by a reaction coordinate uses constrained deterministic or stochastic dynamics. In the literature, constrained Hamiltonian dynamics and overdamped Langevin dynamics have been considered [26,31,41,142]. The gradient of the free energy is obtained from the constraining force or from the Lagrange multipliers used to enforce the constraint. The main disadvantage of Hamiltonian dynamics is their lack of ergodicity; while overdamped Langevin dynamics are rarely used in practice since most codes are based on modifications of the Hamiltonian dynamics. On the other side, the Langevin dynamics is a modification of the Hamiltonian dynamics which can be proved to be ergodic. It is therefore relevant for applications. Our aim in [H29] is precisely to show how to perform thermodynamic integration using Langevin dynamics. Section 2.2.2.2 presents the underlying constrained Langevin dynamics, while the evaluation of the gradient of the free energy is discussed in Section 2.2.2.3.

2.2.2.1 Thermodynamic integration in the alchemical case

We first present thermodynamic integration in the simple context of alchemical transitions when $H_\lambda(q,p) = \frac{1}{2}p^T M^{-1} p + V_\lambda(q)$. Thermodynamic integration consists in remarking that

$$F(1) - F(0) = \int_0^1 F'(\lambda)\, ds, \tag{2.19}$$

and that the derivative

$$F'(\lambda) = \frac{\displaystyle\int_{\mathcal{E}} \frac{\partial H_\lambda}{\partial \lambda}(q,p)\, \mathrm{e}^{-\beta H_\lambda(q,p)}\, dq\, dp}{\displaystyle\int_{\mathcal{E}} \mathrm{e}^{-\beta H_\lambda(q,p)}\, dq\, dp}$$

is the canonical average of $\partial_\lambda H_\lambda = \partial_\lambda V_\lambda$ with respect to the canonical measure

$$\mu_\lambda(dq\, dp) = Z_\lambda^{-1} \mathrm{e}^{-\beta H_\lambda(q,p)}\, dq\, dp. \tag{2.20}$$

In practice, the integral on the right-hand side of (2.19) is discretized in the λ variable by standard quadrature rules to obtain the free energy difference profile. The values $F'(\lambda_i)$ at the quadrature points $\lambda_i \in [0,1]$ are approximated using classical sampling techniques, relying on convergence results such as

$$F'(\lambda) = \lim_{T\to+\infty} \frac{1}{T} \int_0^T \frac{\partial H_\lambda}{\partial \lambda}(q_t, p_t)\, dt \qquad \text{a.s.},$$

where (q_t, p_t) is a realization of the Langevin dynamics

$$\begin{cases} dq_t = M^{-1} p_t\, dt, \\ dp_t = -\nabla V_\lambda(q_t)\, dt - \gamma M^{-1} p_t\, dt + \sqrt{\dfrac{2\gamma}{\beta}}\, dW_t. \end{cases}$$

Some elements on the numerical analysis of the choice of the quadrature points, allowing to minimize the variance of the free energy estimator, can be read in [B1, Section 3.1.1].

2.2.2.2 The constrained Langevin dynamics

We introduce in this section the Langevin dynamics for mechanically constrained systems, for a configuration space $\mathcal{M} = \mathbb{R}^{3N}$. Positions are therefore subjected to a m-dimensional constraint denoted by

$$\xi(q) = (\xi_1(q), \ldots, \xi_m(q))^T = z \in \mathbb{R}^m.$$

Constrained systems appear in computational statistical physics in two types of contexts:

(i) for free energy computations, where ξ is a given reaction coordinate parameterizing a transition between "states" of interest;
(ii) when the system is subjected to molecular constraints such as rigid covalent bonds, or rigid bond angles in molecular systems.

We refer for instance to [123, Chapter 10], [36] and [B1] for applications to the computation of free energy differences, and [7, 74, 105] for mathematical textbooks dealing with constrained Hamiltonian dynamics.

In the sequel, ξ may be thought of as a reaction coordinate (see [H29] for handling additional molecular constraints within the same formalism). The position of the system is constrained to the submanifold $\Sigma(z)$ defined in (2.15) and the associated phase space is denoted by

$$T^*\Sigma(z) = \Big\{(q,p) \in \mathcal{E} \;\Big|\; q \in \Sigma(z),\ \nabla\xi(q)^T M^{-1} p = 0\Big\}. \tag{2.21}$$

Note that the position constraint implicitly places an additional constraint on the momenta, often termed hidden velocity constraint. For a given $q \in \Sigma(z)$, the set of admissible momenta is denoted by

$$T^*_q\Sigma(z) = \Big\{p \in \mathbb{R}^{3N} \;\Big|\; \nabla\xi(q)^T\, M^{-1} p = 0\Big\}. \tag{2.22}$$

The orthogonal projection on $T^*_q\Sigma(z)$ with respect to the scalar product induced by M^{-1} is denoted

$$P_M(q) = \mathrm{Id} - \nabla\xi(q)\, G_M^{-1}(q) \nabla\xi(q)^T M^{-1}, \tag{2.23}$$

where $G_M(q) = \nabla\xi(q)^T M^{-1}\, \nabla\xi(q)$. We assume that G_M is invertible everywhere on $\Sigma(z)$ (for all z). It is easily checked that P_M satisfies the projector property $P_M(q)^2 = P_M(q)$, and the orthogonality property

$$M^{-1} P_M(q) = P_M(q)^T M^{-1}.$$

Finally, it is useful to introduce projected friction and dissipation matrices:

$$(\sigma_P, \gamma_P) = (P_M\, \sigma, P_M\, \gamma\, P_M^T), \tag{2.24}$$

Note that γ_P, σ_P satisfy the fluctuation-dissipation relation (2.8) when γ, σ do.

The canonical distribution associated with constrained systems is defined as

$$\mu_{T^*\Sigma(z)}(dq\, dp) = Z_{z,0}^{-1}\, \mathrm{e}^{-\beta H(q,p)}\, \sigma_{T^*\Sigma(z)}(dq\, dp), \tag{2.25}$$

where $\sigma_{T^*\Sigma(z)}(dq\, dp)$ is the phase space Liouville measure of $T^*\Sigma(z)$ (see [B1, Section 3.3.2] for a precise definition of this measure), and $Z_{z,0}$ the normalizing constant (z refers to the position constraint, and 0 to the velocity or momentum constraint). A dynamics admitting the constrained canonical measure (2.25) as an invariant equilibrium measure is the following Langevin process: For a given initial condition $(q_0, p_0) \in T^*\Sigma(z)$,

$$\text{(CL)} \qquad \begin{cases} dq_t = M^{-1} p_t \, dt, \\ dp_t = -\nabla V(q_t)\, dt - \gamma(q_t) M^{-1} p_t \, dt + \sigma(q_t)\, dW_t + \nabla \xi(q_t)\, d\lambda_t, \\ \xi(q_t) = z, \qquad (C_q) \end{cases}$$

where the $\mathbb{R}^m$-valued adapted process $t \mapsto \lambda_t$ is the Lagrange multiplier associated with the (vectorial) constraint (C_q), and $\gamma(q), \sigma(q)$ are assumed to satisfy the fluctuation-dissipation relation (2.8). Note that $(q_t, p_t) \in T^*\Sigma(z)$ for all $t \geqslant 0$.

Proposition 2.1. *The constrained Langevin dynamics* (CL) *on $T^*\Sigma(z)$ admits the Boltzmann-Gibbs distribution* (2.25) *as a stationary measure. Moreover, if γ_P (defined in* (2.24)*) is everywhere strictly positive in the sense of symmetric matrices on $T^*_q\Sigma(z)$, then the invariant measure is unique and the process* (CL) *is ergodic: for any smooth observable A,*

$$\lim_{T \to +\infty} \frac{1}{T} \int_0^T A(q_t, p_t)\, dt = \int_{T^*\Sigma(z)} A \, d\mu_{T^*\Sigma(z)} \qquad \text{a.s.} \tag{2.26}$$

Several recent studies (*e.g.* [31, 79, 80, 149]) have analyzed dynamics similar to (CL) and some appropriate discretizations of the process in order to approximate the left-hand side of (2.26).

The first contribution of [H29] is to propose a simple discretization of the dynamics (CL) and to highlight its remarkable properties. The numerical scheme is based on a splitting strategy between the Hamiltonian and the fluctuation/dissipation part of the dynamics (in the spirit of the scheme proposed in [20] in the unconstrained case). The Hamiltonian part is discretized using a Verlet scheme with position and momentum constraints (the so-called RATTLE scheme, see [106]). We show that this discretization enjoys the following properties:

(i) for some appropriate choice of the parameters (masses proportional to the time step Δt or friction proportional to Δt^{-1}), the numerical scheme reduces to an Euler discretization of the *overdamped* Langevin dynamics with a projection step associated with the constraints. This can be seen as the numerical counterpart of the fact that the overdamped Langevin dynamics is the limit of the Langevin dynamics as either the friction goes to infinity or the mass goes to zero, see the discussion after (2.9);

(ii) the numerical scheme can be complemented by a Metropolis-Hastings correction [82, 114] to obtain a Generalized Hybrid Monte Carlo (GHMC) method sampling *exactly* (*i.e.* without any bias due to time-discretization) the constrained canonical distribution (2.25). The resulting numerical scheme is close to the ones proposed in [78–80] (see also [47, 109] for historic references on Hybrid Monte Carlo methods, and [88] for GHMC).
The well-posedness of the Metropolis correction crucially relies on reversibility properties of the numerical scheme, here the Hamiltonian part discretized by the RATTLE scheme. Such corrections cannot be considered for standard discretizations of overdamped Langevin dynamics for instance, since the transition kernel corresponding to a single step of the numerical method has no simple analytical expression due to the nonlinear projection step.

One outcome of [H29] is thus a new Metropolization procedure for overdamped Langevin dynamics to sample, without bias, measures supported on a submanifold.

2.2.2.3 Thermodynamic integration with constrained Langevin dynamics

When using constrained simulations in phase space, the momentum variable of the dynamical system is also constrained, and a modified free energy (called "rigid free energy") is more naturally computed:

$$F^M_{\rm rgd}(z) = -\frac{1}{\beta}\ln\int_{T^*\Sigma(z)} \mathrm{e}^{-\beta H(q,p)}\sigma_{T^*\Sigma(z)}(dq\,dp). \tag{2.27}$$

The rigid free energy is related to the standard free energy

$$F(z) = -\frac{1}{\beta}\ln\int_{\Sigma(z)\times\mathbb{R}^{3N}} \mathrm{e}^{-\beta H(q,p)}\,\delta_{\xi(q)-z}(dq)\,dp = -\frac{1}{\beta}\ln\int_{\Sigma(z)} \mathrm{e}^{-\beta V(q)}\,\delta_{\xi(q)-z}(dq) + \mathrm{C} \tag{2.28}$$

used in (2.16) through the identity:

$$F(z) - F^M_{\rm rgd}(z) = -\frac{1}{\beta}\ln\int_{T^*\Sigma(z)} (\det G_M)^{-1/2} d\mu_{T^*\Sigma(z)} + \widetilde{\mathrm{C}}, \tag{2.29}$$

where $\mu_{T^*\Sigma(z)}$ is the equilibrium distribution with constraints (2.25). The constants $\mathrm{C}, \widetilde{\mathrm{C}}$ appearing in the above expressions are independent of z. The relation (2.29) was already proposed in [36] (see also [40, 48, 81, 136] for related formulas). It shows that $F^M_{\rm rgd}$ indeed depends on the mass matrix, which is not obvious in the definition (2.27). For any value of the reaction coordinate, the difference $F(z) - F^M_{\rm rgd}(z)$ can easily be computed with any dynamics sampling from the probability distribution $\mu_{T^*\Sigma(z)}$, such as (CL), by averaging $(\det G_M)^{-1/2}$ along a trajectory.

Several methods have been suggested in the literature to compute either $F^M_{\rm rgd}$ (or similar free energies) from the Lagrange multipliers of a constrained process similar to (CL). In fact, a typical result is that the longtime average of the Lagrange multipliers converges to the gradient of the rigid free energy (2.27) (the so-called mean force). We refer for instance to [36] and references therein for the Hamiltonian case, and to [31] and references therein for the overdamped case. We have also obtained such a result for (CL):

Theorem 2.1. *Assume that $\nabla\xi$, G_M^{-1} and σ are bounded functions on $\Sigma(z)$, and γ_P is strictly positive on $T^*_q\Sigma(z)$ (in the sense of symmetric matrices). Then,*

$$\lim_{T\to+\infty}\frac{1}{T}\int_0^T d\lambda_t = \nabla_z F^M_{\rm rgd}(z) \qquad \text{a.s.} \tag{2.30}$$

A similar result holds for the 'Hamiltonian part' of the Lagrange multipliers:

$$\lim_{T\to+\infty}\frac{1}{T}\int_0^T d\lambda^{\rm ham}_t = \nabla_z F^M_{\rm rgd}(z) \qquad \text{a.s.}, \tag{2.31}$$

where $d\lambda^{\rm ham}_t = d\lambda_t + G_M^{-1}\nabla\xi(q_t)^T M^{-1}\left(-\gamma(q_t)M^{-1}p_t\,dt + \sigma(q_t)dW_t\right) = f^M_{\rm rgd}(q_t,p_t)\,dt$.

The precise expression of $f^M_{\rm rgd}$ is given in [H29]. The important remark is that $d\lambda^{\rm ham}_t$ only has bounded variations since the martingale part due to the Brownian increments and the dissipation term have been subtracted out. Therefore, the estimator based on (2.31) has a smaller variance than the estimator based on (2.30). Similar results on variance reduction were obtained in the overdamped case in [31].

As compared to [36], where a formal proof for the Hamiltonian case is proposed, we use an explicit calculation that does not require the use of the Lagrangian structure of the problem, or a change of coordinates. Once $\nabla_z F^M_{\rm rgd}(z)$ is obtained, $F^M_{\rm rgd}(z)$ can be computed (up to an additive constant) by integration, similarly to what is done in the alchemical case described in Section 2.2.2.1. Note that using (2.30) and thermodynamic integration, together with (2.29), allows to obtain $F(z)$ without computing second order derivatives of ξ. This is a desirable property since computing such high derivatives may be cumbersome for some reaction coordinates used in practice. In contrast, straightforward computations of the mean force using the analytical expression of $f^M_{\rm rgd}$ usually involve such high order derivatives.

We show [H29] that the mean-force can be computed with second order accuracy (*i.e.* up to $\mathrm{O}(\Delta t^2)$ error terms, where Δt is the time-step) using the Lagrange multipliers involved in the Hamiltonian part of the splitting scheme. This is based on a discretization of (2.31), obtained by averaging the two Lagrange multipliers involved in the RATTLE part of the scheme. We also discuss in [H29] how these techniques can be generalized to compute the free energy for systems with molecular constraints.

2.2.3 Nonequilibrium computations of the free energy

This section is devoted to nonequilibrium methods for free energy computations, based on a Hamiltonian or Langevin dynamics with constraints subjected to a predetermined time evolution. Such methods rely on a fluctuation equality, the so-called Jarzynski-Crooks relation (see [93] for a pioneering work, as well as [32,33] for an extension). They are termed "nonequilibrium" since the transition from one value of the reaction coordinate ξ to another one is imposed *a priori*, in a finite time T, and with a given smooth deterministic schedule $t \in [0,T] \mapsto z(t) \in \mathbb{R}^m$. The transition can be arbitrarily fast. Therefore, even if the system starts at equilibrium, it does not remain at equilibrium, in the sense that the law of the process at time t is not the canonical measure associated with the value $z(t)$ of the schedule.

Whereas many works consider nonequilibrium dynamics in the alchemical case, the reaction coordinate case was not treated before our works on nonequilibrium overdamped Langevin dynamics [P6]. Most results of [P6] can in fact be recovered from the results on nonequilibrium Langevin dynamics [H29].

Section 2.2.3.1 first presents the basic idea of nonequilibrium fluctuation relations for computing free energy differences in the simple alchemical case. We then turn to nonequilibrium Langevin dynamics in the reaction coordinate case in Section 2.2.3.2.

2.2.3.1 Principle of the method

The Jarzynski equality expresses free energy differences as a nonlinear average of the work performed in the switching from one state to another, see for instance (2.34) below. The interest of this approach is that the computation of averages such as (2.34) can easily be parallelized using many short trajectories. In practice however, it is often observed that the estimators based on such equalities are numerically inefficient since they have very large variances (see for instance our work [P2] as well as the discussion in [B1, Section 4.1.4]). The interest of the Jarzynski equality and its extensions is therefore rather theoretical.

The Jarzynski equality can easily be obtained for alchemical transitions when the evolution of the system is given by the Hamiltonian dynamics. Consider initial conditions $(q(0),p(0))$ at equilibrium, canonically distributed according to μ_0 (defined in (2.20)), and a switching schedule $\lambda : [0,T] \to \mathbb{R}$ with $\lambda(0) = 0$ and $\lambda(T) = 1$. The evolution is given by the following non-autonomous ordinary differential equation for $0 \leqslant t \leqslant T$:

$$\left\{ \begin{array}{l} \dfrac{dq}{dt}(t) = \ \nabla_p H_{\lambda(t)}(q(t),p(t)), \\ \dfrac{dp}{dt}(t) = -\nabla_q H_{\lambda(t)}(q(t),p(t)). \end{array} \right. \tag{2.32}$$

Defining by ϕ^λ the associated flow, the work performed on the system starting from an initial condition (q,p) is defined through the energy variations induced by the imposed variations of the alchemical parameter:

$$\mathcal{W}(q,p) = \int_0^T \frac{\partial H_{\lambda(t)}}{\partial \lambda}(\phi_t^\lambda(q,p))\, \lambda'(t)\, dt = H_1(\phi_T^\lambda(q,p)) - H_0(q,p). \tag{2.33}$$

The rightmost equality in (2.33) is obtained by noticing that

$$\frac{d}{dt}\Big(H_{\lambda(t)}(\phi_t^\lambda(q,p))\Big) = \frac{\partial H_{\lambda(t)}}{\partial\lambda}(\phi_t^\lambda(q,p))\,\lambda'(t) + \begin{pmatrix}\nabla_q H_{\lambda(t)}(\phi_t^\lambda(q,p))\\ \nabla_p H_{\lambda(t)}(\phi_t^\lambda(q,p))\end{pmatrix}\cdot \partial_t\phi_t^\lambda(q,p),$$

and the second term on the right-hand side vanishes in view of (2.32). The work therefore turns out, in this simple setting, to be equal to the energy difference between the initial and the final states. Then,

$$\int_{\mathcal{E}} \mathrm{e}^{-\beta\mathcal{W}(q,p)}\,d\mu_0(q,p) = Z_0^{-1}\int_{\mathcal{E}} \mathrm{e}^{-\beta H_1(\phi_T^\lambda(q,p))}\,dq\,dp.$$

Since ϕ_T^λ defines a change of variables of Jacobian 1, the above equality can be restated as

$$\mathbb{E}_{\mu_0}\left(\mathrm{e}^{-\beta\mathcal{W}}\right) = \frac{Z_1}{Z_0} = \mathrm{e}^{-\beta(F(1)-F(0))},$$

or

$$F(1) - F(0) = -\frac{1}{\beta}\ln\mathbb{E}_{\mu_0}\left(\mathrm{e}^{-\beta\mathcal{W}}\right), \tag{2.34}$$

where the expectation is taken with respect to initial conditions (q,p) distributed according to μ_0. To approximate numerically (2.34), initial conditions are sampled using an appropriate method, and for each initial condition, a numerical trajectory is integrated in time and the value of the work along this trajectory is computed. Alternatively, dedicated Metropolis algorithms to sample paths can be used (see for instance some algorithms to this end in my work [P9], as well as the discussion in [B1, Section 4.4]).

The relation (2.34) can be generalized to many other dynamics in the alchemical case. The reaction coordinate case is, on the other hand, more technical, and was not considered to our knowledge before our previous work [P6] on switched overdamped Langevin dynamics. The Langevin case is presented in Section 2.2.3.2.

2.2.3.2 Nonequilibrium switching with constrained Langevin dynamics

An appropriate nonequilibrium Langevin dynamics to perform the switching is given by the following equations of motion ("SCL" stands for "switched constrained Langevin"):

$$\text{(SCL)}\qquad \begin{cases} dq_t = M^{-1}p_t\,dt,\\ dp_t = -\nabla V(q_t)\,dt - \gamma_P(q_t)M^{-1}p_t\,dt + \sigma_P(q_t)\,dW_t + \nabla\xi(q_t)\,d\lambda_t,\\ \xi(q_t) = z(t), \qquad\qquad (C_q(t)) \end{cases}$$

where $t\mapsto\lambda_t\in\mathbb{R}^m$ is an adapted process enforcing the constraints $(C_q(t))$ (the Lagrange multipliers). Initial conditions are sampled from the phase-space canonical distribution consistent with the constraints $\xi(q) = z(0)$ and $\nabla\xi(q)^T M^{-1}p = \dot z(0)$. This measure, denoted by $\mu_{\Sigma_\xi, v_\xi}(z(0),\dot z(0))(dq\,dp)$, is made precise in [H29]. For simplicity, we restrict ourselves to projected fluctuation-dissipation matrices of the specific form (2.24) since this simplifies the analysis, and eliminates spurious random fluctuations in the direction of the switching. It also leads to more natural numerical schemes, based again on a splitting procedure.

Our analysis applies to deterministic Hamiltonian dynamics upon choosing $\gamma = 0$. The dynamics (SCL) is a natural extension of the constrained Langevin dynamics (CL). It is different from the dynamics proposed in [101], which is a Langevin dynamics associated with a modified Hamiltonian with projected momenta, driven by a forcing term along $\nabla\xi$ which acts directly on the position variable.

An appropriate notion of work, generalizing the definition (2.33) in the simple case considered in Section 2.2.3.1, is given by the integral of the displacement multiplied by the constraining force:

$$\mathcal{W}_{0,t}\left(\{q_s,p_s\}_{0\leqslant s\leqslant t}\right) := \int_0^t \dot{z}^T(s)\, d\lambda_s. \tag{2.35}$$

Since momenta are implicitly constrained by the condition $\xi(q_t) = z(t)$ for all $t \in [0,T]$ (while, in the "static" definition (2.28) of the free energy, they should not be constrained), some correction term in the spirit of the right-hand side of (2.29) has to be considered in order to state a generalization of the fluctuation identity (2.34) in terms of the free energy $F(z)$ defined in (2.28). More precisely, consider the corrector

$$C(t,q) = \frac{1}{2\beta}\ln\Big(\det G_M(q)\Big) - \frac{1}{2}\dot{z}(t)^T G_M^{-1}(q)\dot{z}(t),$$

where $\frac{1}{2\beta}\ln\det G_M(q)$ is the so-called Fixman term due to the geometry of the position constraints, and $\frac{1}{2}\dot{z}(t)^T G_M^{-1}(q)\dot{z}(t)$ is the kinetic energy term due to the velocity of the switching. We are now in position to state the following result.

Theorem 2.2. *Denote by $\{q_t,p_t\}_{0\leqslant t\leqslant T}$ the solution of the Langevin dynamics* (SCL) *with initial conditions distributed according to $(q_0,p_0) \sim \mu_{\Sigma_\xi,v_\xi}(z(0),\dot{z}(0))(dq\,dp)$. Then,*

$$F(z(T)) - F(z(0)) = -\frac{1}{\beta}\ln\left(\frac{\mathbb{E}\left(\mathrm{e}^{-\beta\left[\mathcal{W}_{0,T}\left(\{q_t,p_t\}_{0\leqslant t\leqslant T}\right)+C(T,q_T)\right]}\right)}{\mathbb{E}\left(\mathrm{e}^{-\beta C(0,q_0)}\right)}\right), \tag{2.36}$$

where the expectations are with respect to canonical (equilibrium) initial conditions and for all realizations of the dynamics (SCL).

Generalizations of (2.36) (fluctuation relations à la Crooks, defined using forward and backward processes, and involving path functionals) are given in [H29].

We also propose in [H29] an original numerical scheme allowing to compute free energy differences without time discretization errors. This numerical scheme is based on a modification of the splitting scheme used to discretize the constrained Langevin dynamics (CL). We are able to prove a discrete-in-time version of the associated Jarzynski free energy estimator (2.36), based on energy differences in the RATTLE steps.

Moreover, for some choice of the parameters, the numerical scheme yields a Jarzynski-Crooks relation similar to (2.36) for an Euler discretization of the overdamped Langevin dynamics with a projection step associated with the evolving constraints, without time discretization error. This can be seen as an extension of the scheme formerly proposed in [P6].

2.3 Sampling constraints in average

This section presents a method to compute properties of systems with constraints fixed in average, proposed in [H15] and applied in [H23] to a real system of interest to physicists. Sampling configurations of systems with constraints fixed in average is also of interest in other applications fields such as polymeric fluids, although the formulation of the problems under consideration are slightly different than (2.43) below (see [104] and references therein).

We make precise in Section 2.3.1 the original physical motivation. The method we have proposed is then described in Section 2.3.2, while numerical results illustrating the approach are provided in Section 2.3.3.

2.3.1 Physical motivation: the computation of Hugoniot curves

When a fluid is hit by a shock wave, its pressure and energy increase. The variations of thermodynamic quantities of interest (pressure, density, energy) across a shock interface are governed by the Rankine-Hugoniot relations, which relate the jumps of the quantities under investigation to the velocity of the shock front. The third Rankine-Hugoniot conservation law for the Euler equation governing the hydrodynamic evolution of the fluid reads (macroscopic quantities are denoted by curly letters)

$$\mathscr{E} - \mathscr{E}_0 - \frac{1}{2}(\mathcal{P} + \mathcal{P}_0)(\mathcal{V}_0 - \mathcal{V}) = 0. \tag{2.37}$$

In this expression, $\mathscr{E}$ is the internal energy of the fluid, $\mathcal{P}$ its pressure, and $\mathcal{V}$ its volume. The subscript 0 refers to the initial state, the other quantities are evaluated after equilibration after the passage of a shock wave. The Hugoniot curve corresponds to all the possible states $(\mathscr{E}, \mathcal{P}, \mathcal{V})$ satisfying (2.37), given $(\mathscr{E}_0, \mathcal{P}_0, \mathcal{V}_0)$. In practice, it is computed by considering shocks of different strengths, inducing various compressions.

A reference temperature T_0 and a simulation cell $\mathcal{D}_0$, for instance $\mathcal{D}_0 = (L_0\mathbb{T})^3$, characterize the equilibrium state before the shock. In numerical experiments, the compression rate

$$c = \frac{|\mathcal{D}|}{|\mathcal{D}_0|}$$

is varied from 1 to some maximal compression rate $0 < c_{\max} < 1$, so that $\mathcal{D} = (c^{1/3}L_0\mathbb{T})^3$ when the compression is isotropic. Since all macroscopic quantities arising in the hydrodynamic equations are obtained thanks to some local thermodynamic equilibrium assumption, (2.37) can be reformulated at the microscopic level using statistical mechanics. For a given compression rate c,

$$\langle H\rangle_{\mathcal{D},T} - \langle H\rangle_{\mathcal{D}_0,T_0} - \frac{1}{2}(\langle P\rangle_{\mathcal{D},T} + \langle P\rangle_{\mathcal{D}_0,T_0})(|\mathcal{D}_0| - |\mathcal{D}|) = 0, \tag{2.38}$$

where the pressure observable for a domain $\mathcal{D}$ is

$$P(q,p) = \frac{1}{3|\mathcal{D}|}\sum_{i=1}^{N}\frac{p_i^2}{m_i} - q_i \cdot \nabla_{q_i} V(q),$$

and the notation $\langle A\rangle_{\mathcal{D},T}$ refers to canonical averages

$$\langle A\rangle_{\mathcal{D},T} = \int_{\mathcal{E}} A(q,p)\,\mu_{\mathcal{D},T}(q,p)\,dq\,dp \tag{2.39}$$

with respect to the canonical measure on $\mathcal{E} = \mathcal{D}^N \times \mathbb{R}^{3N}$

$$\mu_{\mathcal{D},T}(q,p) = \frac{1}{Z_{\mathcal{D},T}}\mathrm{e}^{-\beta H(q,p)}, \qquad Z_{\mathcal{D},T} = \int_{\mathcal{E}} \mathrm{e}^{-\beta H(q,p)}\,dq\,dp, \tag{2.40}$$

with $\beta^{-1} = k_{\mathrm{B}}T$. The final temperature T is the only unknown in (2.38), and is such that

$$\left\langle H(q,p) - \langle H\rangle_{\mathcal{D}_0,T_0} + \frac{1}{2}(P(q,p) + \langle P\rangle_{\mathcal{D}_0,T_0})(1-c)|\mathcal{D}_0| \right\rangle_{\mathcal{D},T} = 0.$$

Introducing the Hugoniot observable (parameterized by the compression parameter c)

$$A_c(q,p) = H(q,p) - \langle H\rangle_{\mathcal{D}_0,T_0} + \frac{1}{2}(P(q,p) + \langle P\rangle_{\mathcal{D}_0,T_0})(1-c)|\mathcal{D}_0|, \tag{2.41}$$

the identification of the thermodynamic states which can be obtained by a shock compression (the so-called Hugoniot problem) can be reformulated as:

$$\text{For a given compression } c_{\max} \leqslant c \leqslant 1, \text{ find } T \text{ such that } \langle A_c \rangle_{c^{1/3}\mathcal{D}_0,T} = 0. \tag{2.42}$$

Once the temperature T is known, the pressure and the internal energy of the fluid can be computed. The compression rate c parameterizes a curve in the (P,T) diagram, called the Hugoniot curve.

Since shock waves propagate in one direction (for instance parallel to the x axis), anisotropic versions of the Hugoniot problem are of interest. In this case, the compression acts in the x direction only, and $\mathcal{D} = cL_0\mathbb{T} \times (L_0\mathbb{T})^2$. This is relevant when the initial state before the shock compression is in a solid phase. The average pressure P is replaced by the P_{xx} component of the pressure tensor:

$$P_{xx}(q,p) = \frac{1}{|\mathcal{D}|}\sum_{i=1}^{N}\frac{p_{i,x}^2}{m_i} - q_{i,x}\partial_{q_{i,x}}V(q),$$

where $q_{i,x}, p_{i,x}$ respectively denote the x components of the position and momentum of the i-th particle, and the observable A_c is replaced by

$$A_{xx,c}(q,p) = H(q,p) - \langle H\rangle_{\mathcal{D}_0,T_0} + \frac{1}{2}(P_{xx}(q,p) + \langle P_{xx}\rangle_{\mathcal{D}_0,T_0})(1-c)|\mathcal{D}_0|.$$

Again, the issue is to find the temperature T such that $\langle A_{c,xx}\rangle_{\mathcal{D},T} = 0$ for given $\mathcal{D}$.

2.3.2 A nonlinear dynamics to sample constraints in average

In the sequel we focus on constraints depending on the temperature T, and therefore drop the mention of the volume in the notation of the canonical averages when it is not relevant. Constraints on the volume can be handled similarly. An abstract reformulation of questions such as (2.42) reads: for a given observable A,

$$\text{find } T \text{ such that } \langle A\rangle_T = 0. \tag{2.43}$$

In order to have a well-defined problem (and possibly upon replacing A by $-A$), we assume in the sequel that (2.43) has a unique solution T^* and that, at least locally around T^*,

$$0 < \alpha \leqslant \frac{\langle A\rangle_T - \langle A\rangle_{T^*}}{T - T^*} \leqslant a. \tag{2.44}$$

This assumption on the observable is satisfied as soon as the derivative of $T \mapsto \langle A\rangle_T$ is smooth and does not vanish at T^*. For simplicity, we also assume that A, V are smooth (see [H15] for precise conditions).

Several ways of solving (2.43) have been proposed in the literature. The first one relies on a Newton-like strategy, in which case the derivative of the function $T \mapsto \langle A\rangle_T$ should be computed with a good accuracy. This is a non trivial task since this derivative is approximated in practice by a finite difference $(\langle A\rangle_{T+\Delta T} - \langle A\rangle_{T-\Delta T})/2\Delta T$, so that the statistical error inherent in the numerical approximation of the quantities $\langle A\rangle_{T\pm\Delta T}$ should be sufficiently small compared to ΔT. This requires a substantial computational effort. A second strategy is to resort to dedicated dynamics, with some appropriate feedback mechanism to increase or decrease the energy of the system depending on the current value of A (see [111]). However, the invariant measure of the corresponding dynamics is not known, and so it is unclear in which sense (2.43) is satisfied.

In the dynamics we propose in [H15], the temperature is a variable and the state of the system is described by the variables (q,p,T). The idea is that the update of the current configuration (q,p) is governed by a dynamics consistent with canonical sampling at the instantaneous temperature $T(t)$, while the temperature is updated depending on the current estimate of $\langle A\rangle_{T(t)}$: the temperature

is decreased if the estimate is positive, increased otherwise. For instance, consider the following dynamics of overdamped Langevin type:

$$\begin{cases} dq_t &= -\nabla V(q_t)\,dt + \sqrt{2k_{\mathrm{B}}T(t)}\,dW_t, \\ T'(t) &= -\gamma\,\mathbb{E}(A(q_t)), \end{cases} \tag{2.45}$$

or the corresponding Langevin version:

$$\begin{cases} dq_t &= M^{-1}p_t\,dt, \\ dp_t &= -\nabla V(q_t)\,dt - \xi M^{-1}p_t\,dt + \sqrt{2\xi k_{\mathrm{B}}T(t)}\,dW_t, \\ T'(t) &= -\gamma\,\mathbb{E}(A(q_t,p_t)), \end{cases} \tag{2.46}$$

for some friction parameter $\xi > 0$. In both cases, $\gamma > 0$ determines the time scale of the temperature feedback term, and W_t is a standard $3N$-dimensional Brownian motion. To prove mathematical results, it is convenient to use an overdamped Langevin dynamics, since the associated Fokker-Planck equation describing the evolution of the law of the process q_t is parabolic. However, we use the hypoelliptic Langevin dynamics in numerical applications since this dynamics is more commonly used in molecular simulation codes. Using tools of hypoellipticity and hypocoercivity (see [150]), it should be possible to prove results similar to Theorems 2.3 and 2.4 below when the underlying dynamics is of Langevin type.

The dynamics (2.45) and (2.46) can be motivated as follows. If the configurations followed adiabatically the temperature changes, the positions q_t (and possibly the momenta p_t) would be distributed canonically at the temperature $T(t)$ at all times, and $T'(t) = -\gamma\,\langle A\rangle_{T(t)}$. The condition (2.44) then implies $-\gamma a(T(t)-T^*) \leqslant T'(t) \leqslant -\gamma\alpha(T(t)-T^*) \leqslant 0$ if $T(0) > T^*$, and a similar inequality if $T(0) < T^*$. In any case, $T(t) \to T^*$ exponentially fast.

Now, the positions are not canonically distributed at all times since the temperature varies at a finite rate. The hope is that, even if equilibrium is not maintained at all times, the nonlinear dynamics can still converge if the typical time arising in the temperature update is sufficiently small compared to the typical relaxation time of spatial part of the dynamics on q, p. These heuristic considerations can be quantified using functional inequalities, see Theorem 2.4 below.

2.3.2.1 Well-posedness of the dynamics

Let us first show that the dynamics (2.45) is well posed. This is not clear *a priori* since the temperature $T(t)$ should remain nonnegative. To this end, we consider a weak formulation of (2.45). The Fokker-Planck equation describing the evolution of the law of the process reads

$$\begin{cases} \partial_t\psi &= k_{\mathrm{B}}T(t)\,\nabla\cdot\left[\mu_{T(t)}\nabla\left(\dfrac{\psi}{\mu_{T(t)}}\right)\right] = k_{\mathrm{B}}T(t)\,\Delta\psi + \nabla\cdot(\psi\nabla V), \\ T'(t) = -\gamma\displaystyle\int_{\mathcal{D}^N} A(q)\psi(t,q)\,dq, \end{cases} \tag{2.47}$$

where the periodic function $q \in \mathcal{D}^N \mapsto \psi(t,q)$ is the law of the process q_t at time t, and

$$\mu_T(q) = Z_T^{-1}\exp\left(-\frac{V(q)}{k_{\mathrm{B}}T}\right). \tag{2.48}$$

The well-posedness of (2.47) for short times is given by the following result, whose proof is based upon an appropriate application of the Schauder fixed point theorem.

Theorem 2.3. *For a given initial condition (T^0, ψ^0), with $T^0 > 0$ and*

$$\psi^0 \in H^2(\mathcal{D}^N), \qquad \psi^0 \geqslant 0, \qquad \int_{\mathcal{D}^N} \psi^0 = 1,$$

there exists a time $\tau \geqslant \dfrac{T^0}{2\gamma\|A\|_\infty} > 0$ *such that* (2.47) *has a unique solution* (T, ψ) *with* $T \in C^1([0,\tau], \mathbb{R}_+)$ *and* $\psi \in C^0([0,\tau], H^2(\mathcal{D}^N))$. *Moreover,* $\psi \geqslant 0$, *and* $\psi > 0$ *when* $\psi^0 > 0$.

2.3.2.2 Convergence to the target temperature

To study the convergence of the nonlinear dynamics (2.47) under its formulation as a partial differential equation, entropy methods can be used (see for instance the review papers [6,70]). The total entropy we consider here is the sum of a spatial entropy $E(t)$, related to the distribution of configurations at time t, and a temperature term:

$$\mathcal{E}(t) = E(t) + \frac{1}{2}(T(t) - T^*)^2,$$

with

$$E(t) = \int_{\mathcal{D}^N} h\left(f(t)\right) \mu_{T(t)}, \qquad f(t) = \frac{\psi(t,\cdot)}{\mu_{T(t)}}, \qquad h(x) = x\ln x - x + 1. \tag{2.49}$$

Note that the reference measure $\mu_{T(t)}$ is time-dependent. If $\mathcal{E}(t) \to 0$ as $t \to +\infty$, then $T(t) \to T^*$ and $\psi(t) \to \mu_{T^*}$.

A typical convergence result can be stated for initial data not too far from the fixed point (T^*, μ_{T^*}), provided that the canonical measure satisfies some functional inequalities. Roughly speaking, these functional inequalities mean that the dynamics at a fixed temperature converges sufficiently fast to equilibrium.

Assumption 2.1. *There exists an interval* $I_T^{\mathrm{LSI}} = [T_{\min}^{\mathrm{LSI}}, T_{\max}^{\mathrm{LSI}}]$ *(with* $T_{\min}^{\mathrm{LSI}} > 0$ *and* $T_{\min}^{\mathrm{LSI}} < T^* < T_{\max}^{\mathrm{LSI}}$*) such that the family of measures* $\{\mu_T\}_{T \in I_T^{\mathrm{LSI}}}$ *satisfies a logarithmic Sobolev inequality (LSI) with a uniform constant* $1/\rho$, *namely*

$$\int_{\mathcal{D}^N} h(f)\mu_T \leqslant \frac{1}{\rho}\int_{\mathcal{D}^N} \frac{|\nabla f|^2}{f}\,\mu_T.$$

A LSI holds for instance in the following cases: when the potential V satisfies a strict convexity condition of the form $\mathrm{Hess}(V) \geqslant \nu\,\mathrm{Id}$ with $\nu > 0$ (as a special case of the Bakry and Emery criterion [10]), or when the measure μ_T is a tensorization of measures satisfying a LSI (see Gross [68]). Moreover, when a LSI with constant ρ is satisfied by $Z_V^{-1}\,\mathrm{e}^{-V(q)}\,dq$, then $Z_{V+W}^{-1}\,\mathrm{e}^{-(V(q)+W(q))}\,dq$ (with W bounded) satisfies a LSI with constant $\tilde{\rho} = \rho\,\mathrm{e}^{\inf W - \sup W}$. This property expresses some stability with respect to bounded perturbations (see Holley and Stroock [87]). In particular, the canonical measure associated with smooth potentials on a compact state space (as is the case here) satisfies a LSI. The uniformity of the constant can be ensured by restricting the temperatures to a finite interval isolated away from 0.

Theorem 2.4. *Consider an initial data* (T^0, ψ^0) *with* $\psi^0 \in H^2(\mathcal{D}^N)$, $\psi^0 \geqslant 0$, $\displaystyle\int_{\mathcal{D}^N} \psi^0 = 1$, *and associated entropy* $\mathcal{E}(0) \leqslant \mathcal{E}^*$, *where*

$$\mathcal{E}^* = \inf\left\{\frac{1}{2}(T_{\min}^{\mathrm{LSI}} - T^*)^2, \frac{1}{2}(T_{\max}^{\mathrm{LSI}} - T^*)^2\right\}.$$

Then, there exists $\gamma_0 > 0$ *such that, for all* $0 < \gamma \leqslant \gamma_0$, (2.47) *has a unique solution* $(T, \psi) \in C^1(\mathbb{R}_+, \mathbb{R}) \times C^0(\mathbb{R}_+, H^2(\mathcal{D}^N))$, *and the entropy converges exponentially fast to zero: There exists* $\kappa > 0$ *(depending on* γ*) such that*

$$\mathcal{E}(t) \leqslant \mathcal{E}(0) \exp(-\kappa t).$$

In particular, the temperature remains positive at all times: $T(t) \geqslant T_{\min}^{\mathrm{LSI}} > 0$, *and it converges exponentially fast to* T^*.

The proof of this result follows from a Gronwall inequality on the entropy $E(t)$, which, in turn, is a consequence of the assumed uniform LSI and some algebraic computations to control the time derivatives of the temperature. These computations allow to give an expression of the critical temperature update rate γ_0 and the exponential decay rate κ in terms of the the LSI rate ρ and other parameters of the model ($\|A\|_\infty, \|V\|_\infty, T_{\min}^{\mathrm{LSI}}$).

An alternative convergence result can be stated provided a Poincaré inequality holds (which is a weaker statement than LSI) under a smallness condition on the L^2 entropy of the initial data (corresponding to the choice $h(x) = \frac{1}{2}(x-1)^2$ in (2.49)).

2.3.3 Some numerical results

We applied the proposed method (2.46), with expectations approximated by appropriate time averages along a single trajectory, to a model Lennard-Jones fluid, using the code S-TAMP from CEA/DAM (see the extensive numerical results presented in [H15]). We discussed in particular the choice of the parameters, with a focus on the rate γ at which the temperature is modified. As expected (and as predicted by Theorem 2.4), the convergence is slower for small values of γ (the temperature is not updated fast enough), whereas larger frequencies trigger fast initial oscillations in the temperature which may lead to numerical instabilities in the scheme. We present in Figure 2.2 typical time evolutions of the temperature for a given compression rate (left) and a typical Hugoniot curve obtained from computations at various compression rates (right).

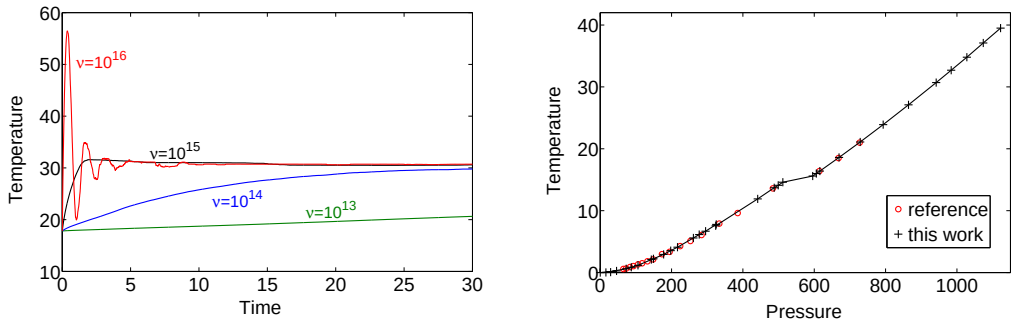


Fig. 2.2. Left: Plot of the temperature as a function of time (in reduced units) for various values of the frequency $\nu = Nk_{\mathrm{B}}\gamma$ (in s^{-1}), for a system of size $N = 4,000$ and a given compression rate. Right: Hugoniot curve for Argon (in reduced units, solid line and crosses). The reference results from [111] are also reported (circles).

We have also applied the method in [H23] to compute the Hugoniot curve of TATB, a material of interest for the physicists at CEA/DAM, before and after the passage of a detonation wave. In this case, the underlying dynamics is a discrete Metropolis algorithm [114] rather than a Langevin dynamics.

3

Nonequilibrium systems and transport properties

This chapter is devoted to theoretical results and numerical methods for steady-state nonequilibrium systems in computational statistical physics. Section 3.1 recalls the general framework of linear response for nonequilibrium perturbations of equilibrium dynamics. Section 3.2 then presents some results related to thermal transport in one dimensional chains (see our works [H16, H18, H22, H24, H28]); while Section 3.3, based on [H26], focuses on the computation of the shear viscosity.

3.1 Nonequilibrium systems and linear response theory

The aim of this section is to provide a general introduction to linear response theory for nonequilibrium perturbations of equilibrium systems. Section 3.1.1 discusses general features of nonequilibrium dynamics. Nonequilibrium perturbations of equilibrium dynamics are then considered in Section 3.1.2. We introduce in particular two prototypical examples which illustrate our abstract presentation throughout this section: the self-diffusion of a particle and the thermal transport in one dimensional chains. Linear response is then studied in Section 3.1.3, where we provide in particular a formal expression for the invariant probability measure of the system and connect the computation of transport properties to appropriate correlation functions.

3.1.1 Equilibrium and nonequilibrium dynamics

Nonequilibrium systems are characterized, from a physical viewpoint, by the irreversibility of their evolutions. We consider in this chapter dynamics in their steady-states. The irreversibility then often manifests itself through the existence of non-zero fluxes or currents flowing from one part of the system to another one. To create and maintain such fluxes, an appropriate external forcing has to be applied. To study thermal transport for instance, a typical set-up is to maintain two parts of the system at different temperatures, henceforth creating an energy flux from the hottest to the coldest region. Of course, to reach some steady-state, some dissipation mechanism has to be considered as well, otherwise the external forcing may lead to an uncontrolled growth of the energy of the system.

In order to give a mathematical definition of steady-state nonequilibrium systems complementing the above physical picture, we need to introduce a few notions. We consider in this introductory section a general stochastic dynamics on a configuration space $\mathcal{X}$ (typically, the configuration space $\mathbb{R}^{3N}$ or $\mathbb{T}^{3N}$ when $x = q$, or the phase-space $\mathbb{R}^{3N} \times \mathbb{R}^{3N}$ or $\mathbb{T}^{3N} \times \mathbb{R}^{3N}$ when $x = (q, p)$):

$$dx_t = b(x_t)\, dt + \sigma(x_t)\, dW_t, \tag{3.1}$$

where W_t is a standard Brownian motion. Recall that invariant measures of such processes are stationary solutions of the Fokker-Planck equation (2.5) associated to (3.1) (see the introduction of Chapter 2). The existence and uniqueness of an invariant probability measure with a smooth density for the process (3.1) can be proved for instance by the techniques reviewed in [128].

From a mathematical viewpoint, equilibrium systems are characterized by the self-adjointness of the generator $\mathcal{A}$ (defined in (2.6)) on the weighted Hilbert space $L^2(\psi_\infty)$, where ψ_∞ is the density of the (unique) invariant probability measure of the dynamics:

$$\int_{\mathcal{X}} \mathcal{A}f\, g\, \psi_\infty = \int_{\mathcal{X}} f\, \mathcal{A}g\, \psi_\infty. \tag{3.2}$$

This expresses the reversibility of the dynamics with respect to the invariant measure of the process. In some cases, such a reversibility property holds only up to a one-to-one transformation preserving the invariant measure. For example, for the Langevin dynamics, whose generator and invariant probability measure respectively read

$$\mathcal{A} = M^{-1}p \cdot \nabla_p - \nabla V \cdot \nabla_p - \gamma M^{-1}p \cdot \nabla_p + \frac{1}{\beta}\Delta_p, \qquad \psi_\infty(q,p)\, dq\, dp = Z^{-1}\mathrm{e}^{-\beta H(q,p)}\, dq\, dp,$$

reversibility is valid only upon momentum reversal $S(q, p) = (q, -p)$:

$$\int_{\mathcal{E}} \mathcal{A}f\, g\, \psi_\infty = \int_{\mathcal{E}} (f \circ S)\mathcal{A}(g \circ S)\, \psi_\infty. \tag{3.3}$$

Reversibility properties such as (3.2) or (3.3) are no longer true for nonequilibrium dynamics.

An important property of nonequilibrium systems is that their invariant measures in general depend non-trivially on the details of the dynamics. This is not the case for equilibrium dynamics. Indeed, consider for instance the overdamped Langevin dynamics on the compact configuration space $\mathbb{T}^d = (\mathbb{R}\backslash\mathbb{Z})^d$

$$dx_t = -\nabla V(x_t)\,dt + \sqrt{\frac{2}{\beta}}\,dW_t, \tag{3.4}$$

for a smooth periodic potential V. Its unique invariant probability measure is $Z^{-1}\mathrm{e}^{-\beta V(x)}\,dx$. Now, if the dynamics (3.4) is perturbed by a smooth gradient modification of the drift term as

$$dx_t = \Big(-\nabla V(x_t) + \nabla\widetilde{V}(x_t)\Big)dt + \sqrt{\frac{2}{\beta}}\,dW_t, \tag{3.5}$$

then the unique invariant measure becomes $\mathrm{e}^{-\beta(V(x)-\widetilde{V}(x))}\,dx$. In particular, the invariant measure is modified only on the support of the perturbation $\widetilde{V}$. For nonequilibrium dynamics (for instance, when b does not derive from a gradient), the invariant measure is in general modified everywhere even if the perturbation is restricted to a small domain. This is due to long-range correlations which are generically present in nonequilibrium systems (see for instance [42]). Let us illustrate these physical considerations by a simple analytical example (taken from [127, Section 2.5]). Consider the dynamics (3.4) perturbed by a force which is not the gradient of a periodic potential, in dimension $d = 1$ and in the case $\beta = 1$:

$$dx_t = \Big(-V'(x_t) + F\Big)dt + \sqrt{2}\,dW_t,$$

where $F \in \mathbb{R}\backslash\{0\}$ is a constant force. Standard techniques (see again [128]) allow to show the existence and uniqueness of an invariant probability measure $\psi_\infty(x)\,dx$, which satisfies the stationary Fokker-Planck equation

$$\frac{d}{dx}\left((V' - F)\psi_\infty + \frac{d\psi_\infty}{dx}\right) = 0. \tag{3.6}$$

In fact, it can be checked that the periodic function

$$\psi_\infty(x) = Z^{-1}\mathrm{e}^{-V(x)+Fx}\int_x^{x+1}\mathrm{e}^{V(y)-Fy}\,dy = Z^{-1}\int_0^1\mathrm{e}^{V(x+y)-V(x)-Fy}\,dy,$$

with Z chosen such that $\int_0^1\psi_\infty = 1$, indeed satisfies (3.6). It is clear from the expression of the invariant measure that, even if the potential V is only locally perturbed by some potential $\widetilde{V}$, the invariant measure is in general modified everywhere on $\mathbb{T}$.

3.1.2 Nonequilibrium perturbations of equilibrium dynamics

We consider in this chapter nonequilibrium perturbations of equilibrium dynamics, through:

(i) the addition of non-gradient forces as in Section 3.3, a prototypical example being given in Section 3.1.2.1;
(ii) fluctuation terms with different temperatures, an example being thermal transport in one-dimensional chains (Section 3.1.2.2).

These perturbations of equilibrium dynamics are introduced to compute a transport coefficient α, which relates the magnitude of the response of the system in its steady-state (an average current) to the magnitude of the external forcing (see (3.18) below).

Recall that there are three main types of techniques to compute transport properties:

(i) *equilibrium techniques* based on Green-Kubo formulas, which are integrated correlation functions of the general form

$$\alpha = \int_0^{+\infty} \mathbb{E}\Big(A(x_t)B(x_0)\Big)\, dt,$$

where A, B are two appropriate observables, and where the expectation is taken with respect to all initial conditions distributed according to the invariant probability measure of some reference dynamics, and for all realizations of this dynamics;

(ii) *transient methods*, where the system is initially locally perturbed, and the relaxation of this perturbation is monitored as a function of time. The comparison with the assumed macroscopic evolution equation (for instance the heat equation for thermal transport) allows to identify the physical parameters of the macroscopic evolution (such as the thermal conductivity); see [89, 143] for an application of this technique.

(iii) *steady-state nonequilibrium techniques* where a forcing is permanently applied to the system. The latter methods can be decomposed into two subcategories: boundary driven techniques where the external forcing is imposed only in boundary regions, and bulk driven dynamics where the perturbation is experienced by all particles in the system. In both cases, an appropriate flux is measured, and the transport coefficient is obtained as the ratio of the average flux to the magnitude of the external forcing. The expression of the flux function is again defined in analogy with macroscopic thermodynamics.
Bulk dynamics are often numerically more efficient since the forcing is applied globally to the system, and therefore the steady state can be reached faster. Besides, it is in general impossible to prove the existence and uniqueness of an invariant probability measure for boundary driven dynamics, except in very simple geometries such as one dimensional atom chains.

It should be emphasized that the definition of transport coefficients is based on an analogy with macroscopic evolution equations. This is clear for transient and steady states dynamics. It is in fact also the case for equilibrium methods since the expression of the transport coefficient as some correlation function can be seen as a reformulation of the linear response result for steady state nonequilibrium dynamics (see (3.19) below).

3.1.2.1 Non-gradient perturbations

Consider the following dynamics for a system in a periodic potential V:

$$\begin{cases} dq_t = M^{-1} p_t \, dt, \\ dp_t = \Big(- \nabla V(q_t) + \xi F \Big) dt - \gamma M^{-1} p_t \, dt + \sqrt{\dfrac{2\gamma}{\beta}} \, dW_t, \end{cases} \tag{3.7}$$

where $(q_t, p_t) \in \mathbb{T}^d \times \mathbb{R}^d$ and $F \in \mathbb{R}^d$. Note that a non-zero constant force F does not derive from a periodic potential.

It is expected, from a physical viewpoint, that the application of a non-zero constant force in a given direction induces a non-zero velocity in this direction. The relevant response of the system is therefore chosen to be the observable

$$R(q,p) = F \cdot M^{-1} p. \tag{3.8}$$

This allows to define the mobility as the ratio of the average projected velocity R divided by ξ, in the limit of small forcings (see (3.20) below).

3.1.2.2 Fluctuation terms with different temperatures

Consider a one dimensional chain of N atoms of equal masses 1, with positions $q = (q_1, \ldots, q_N)$ and momenta $p = (p_1, \ldots, p_N)$. The left end of the chain is attached to a wall ($q_0 = 0$ and $p_0 = 0$

at all times), while the right end is free. Attaching the chain on one side is important to remove the translation invariance of the whole system. Denoting by v the interaction potential among the atoms when only nearest neighbor interactions are considered, the Hamiltonian reads

$$H(q,p) = \sum_{i=1}^{N} \frac{p_i^2}{2} + V(q), \qquad V(q) = v(q_1) + \sum_{i=1}^{N-1} v(q_{i+1} - q_i). \tag{3.9}$$

The evolution is governed by the Hamiltonian dynamics in the bulk (that is, for $i \in \{2, \dots, N-1\}$), and Langevin dynamics at the two ends of the chain in order to impose temperatures $T_{\mathrm{L}}, T_{\mathrm{R}}$ at the left and right boundaries respectively:

$$\begin{cases} dq_i = p_i\, dt, \\ dp_i = \Big(v'(q_{i+1} - q_i) - v'(q_i - q_{i-1})\Big) dt, \qquad i \neq 1, N, \\ dp_1 = \Big(v'(q_2 - q_1) - v'(q_1)\Big) dt - \gamma p_1\, dt + \sqrt{2\gamma T_{\mathrm{L}}}\, dW_t^1, \\ dp_N = -v'(q_N - q_{N-1})\, dt - \gamma p_N\, dt + \sqrt{2\gamma T_{\mathrm{R}}}\, dW_t^N, \end{cases} \tag{3.10}$$

where $\gamma > 0$ is the intensity of the thermostats.

The existence and uniqueness of a smooth invariant probability measure for the dynamics (3.10) can be proved under appropriate assumptions on the interaction potential v. In particular, some (super)quadratic growth at infinity is required. Such results are based either on methods from spectral theory [49, 51] (in which case some additional pinning potential of the form $u(q_i)$, with u growing sufficiently fast at infinity, is required at each site), or on probabilistic techniques [25, 50, 130, 131]. In all cases, it is shown that the generator of the dynamics has a compact resolvent in an appropriate Hilbert space. When $T_{\mathrm{L}} = T_{\mathrm{R}} = T$, this invariant probability measure is the Gibbs measure at inverse temperature $\beta^{-1} = k_{\mathrm{B}}T$. When $T_{\mathrm{L}} \neq T_{\mathrm{R}}$, there is in general no simple expression of the invariant measure. Note that there are also situations such as the one studied in [75] where the existence of an invariant probability measure is not known. The main obstruction is the lack of a spectral gap in the spectrum of the generator.

When $T_{\mathrm{L}} \neq T_{\mathrm{R}}$, an energy flow through the system from the cold to the hot region is expected. This can be proved by computing the entropy production in the system [15, 50]. The thermal conductivity is defined as the energy flux divided by the temperature difference (see (3.21) below). The relevant physical response of the system is the total energy current J across the system

$$J(q,p) = \sum_{i=1}^{N-1} j_{i+1,i}(q,p), \qquad j_{i+1,i}(q,p) = -v'(q_{i+1} - q_i)\frac{p_i + p_{i+1}}{2}, \tag{3.11}$$

which is the sum of the local currents $j_{i,i-1}$ expressing the local conservation of the energy. The expression of these currents is motivated as follows. Consider an index $i = 2, \dots, N-1$. The energy ε_i at the i-th site is the sum of the kinetic energy and half of the interaction energies with the neighboring sites:

$$\varepsilon_i(q,p) = \frac{p_i^2}{2} + \frac{1}{2}\Big(v(q_{i+1} - q_i) + v(q_i - q_{i-1})\Big), \tag{3.12}$$

with appropriate modifications at the boundaries:

$$\varepsilon_1(q,p) = \frac{p_1^2}{2} + v(q_1) + \frac{1}{2}v(q_2 - q_1), \qquad \varepsilon_i(q,p) = \frac{p_N^2}{2} + \frac{1}{2}v(q_N - q_{N-1}).$$

A simple computation shows that the variation of the local energy in the bulk ($2 \leqslant i \leqslant N-1$) is given by the following conservation law:

$$d\varepsilon_i = \Big(j_{i,i-1} - j_{i+1,i}\Big)dt.$$

The quantities $j_{i,i-1}$ can therefore be interpreted as energy fluxes from the site $i-1$ to the site i.

3.1.3 Linear response for nonequilibrium dynamics

We present in this section a formal study of nonequilibrium dynamics that are perturbations of equilibrium processes. The various assumptions we make need to be justified for the particular dynamics considered in applications.

3.1.3.1 Reference equilibrium dynamics

We denote by $\mathcal{A}_0$ the generator of the reference equilibrium dynamics on the state-space $\mathcal{X}$, and by ψ_0 its invariant measure, which is assumed to be unique. The generator of the perturbation is $\mathcal{A}_1$, so that the generator of the nonequilibrium dynamics reads $\mathcal{A}_0 + \xi\mathcal{A}_1$.

Let us give the expressions of the above quantities for the two examples presented in Section 3.1.2:

(i) For the dynamics (3.7), the generator of the reference dynamics (corresponding to the case $F = 0$) and of the perturbation respectively read

$$\mathcal{A}_0 = M^{-1}p \cdot \nabla_p - \nabla V \cdot \nabla_p - \gamma M^{-1}p \cdot \nabla_p + \frac{\gamma}{\beta}\Delta_p, \qquad \mathcal{A}_1 = F \cdot \partial_p. \tag{3.13}$$

The invariant probability measure is

$$\psi_0(q,p)\,dq\,dp = Z^{-1}\exp\left(-\beta\left[\frac{1}{2}p^T M^{-1}p + V(q)\right]\right)\,dq\,dp. \tag{3.14}$$

(ii) Consider now the dynamics (3.10) with $T_{\rm L} = T + \Delta T$ and $T_{\rm R} = T - \Delta T$. We set $\xi = \Delta T$. The reference equilibrium dynamics is the Langevin dynamics (3.10) with the two thermostats at the boundaries at the same temperature T. Its generator reads

$$\mathcal{A}_0 = \sum_{i=1}^{N} p_i\partial_{q_i} - (\partial_{q_i}V)\,\partial_{p_i} - \gamma\Big(p_1\partial_{p_1} + p_N\partial_{p_N}\Big) + \gamma T\Big(\partial_{p_1}^2 + \partial_{p_N}^2\Big), \tag{3.15}$$

and the invariant probability measure has a density $\psi_0(q,p) = Z^{-1}\mathrm{e}^{-H(q,p)/T}$, where H is given by (3.9). The generator of the perturbation is $\mathcal{A}_1 = \gamma(\partial_{p_1}^2 - \partial_{p_N}^2)$.

3.1.3.2 Invariant measure of the nonequilibrium dynamics

Denote by ψ_ξ the density of the invariant measure of the nonequilibrium dynamics (assuming that it exists). We also assume that the invariant measure is unique. Recall that some techniques to prove existence and uniqueness of invariant measures are reviewed in [128]. The function ψ_ξ is the stationary solution of the Fokker-Planck equation. Equivalently, ψ_ξ is defined by the following requirement:

$$\int_{\mathcal{X}} \Big(\mathcal{A}_0 + \xi\mathcal{A}_1\Big)\varphi\,\psi_\xi = 0$$

for all test functions φ. It is convenient to write ψ_ξ as a perturbation of the reference measure:

$$\psi_\xi = f_\xi\,\psi_0,$$

and to work on the Hilbert space $L^2(\psi_0)$ endowed with the scalar product

$$\langle f, g \rangle_{L^2(\psi_0)} = \int_{\mathcal{X}} f(x) g(x)\, \psi_0(x)\, dx.$$

The function f_ξ is then the unique solution of the Fokker-Planck equation

$$(\mathcal{A}_0^* + \xi \mathcal{A}_1^*)\, f_\xi = 0, \qquad \int_{\mathcal{E}} f_\xi \psi_0 = 1, \tag{3.16}$$

where adjoints are considered on $L^2(\psi_0)$. Note that the invariance of the reference measure ψ_0 is expressed in this framework as

$$\mathcal{A}_0^* \mathbf{1} = 0.$$

The uniqueness of the reference invariant measure ψ_0 means that $\mathrm{Ker}(\mathcal{A}_0^*) = \mathrm{Span}(\mathbf{1})$. It is useful to introduce the Hilbert space

$$\mathcal{H} = \left\{ f \in L^2(\psi_0) \;\middle|\; \int_{\mathcal{X}} f \psi_0 = 0 \right\} = L^2(\psi_0) \cap \{\mathbf{1}\}^\perp,$$

where the orthogonality is understood with respect to the $L^2(\psi_0)$ scalar product.

The following result gives the expression of the function f_ξ as a power series in ξ when ξ is sufficiently small, under appropriate assumptions on the perturbation $\mathcal{A}_1$.

Theorem 3.1. *Assume that* (3.16) *has a unique solution, and that*

(a) (properties of the equilibrium dynamics) $\mathrm{Ker}(\mathcal{A}_0^*) = \mathbf{1}$ *and* $\mathcal{A}_0^*$ *is invertible on* $\mathcal{H}$*;*
(b) (properties of the perturbation) $\mathrm{Ran}(\mathcal{A}_1^*) \subset \mathcal{H}$ *and* $(\mathcal{A}_0^*)^{-1} \mathcal{A}_1^*$ *is bounded on* $\mathcal{H}$*.*

Denote by r *the spectral radius of the bounded operator* $(\mathcal{A}_0^*)^{-1} \mathcal{A}_1^* \in \mathcal{B}(\mathcal{H})$*:*

$$r = \lim_{n \to +\infty} \left\| \left((\mathcal{A}_0^*)^{-1} \mathcal{A}_1^* \right)^n \right\|^{1/n}.$$

Then, for $|\xi| < r^{-1}$*, the unique solution of* (3.16) *can be written as*

$$f_\xi = \left(1 + \xi\, (\mathcal{A}_0^*)^{-1} \mathcal{A}_1^* \right)^{-1} \mathbf{1} = \left(1 + \sum_{n=1}^{+\infty} (-\xi)^n \left[(\mathcal{A}_0^*)^{-1} \mathcal{A}_1^* \right]^n \right) \mathbf{1}. \tag{3.17}$$

The linear term in ξ in the expression of f_ξ is denoted by

$$\mathrm{f}_1 = -\, (\mathcal{A}_0^*)^{-1} \mathcal{A}_1^* \mathbf{1}.$$

Note that the measure (3.17) is a probability measure: the normalization constant for ψ_ξ does not depend on ξ. This owes to the fact that $\mathrm{Ran}((\mathcal{A}_0^*)^{-1} \mathcal{A}_1^*) \subset \mathcal{H}$, and

$$\int_{\mathcal{X}} h \psi_0 = 0$$

for any $h \in \mathcal{H}$, so that

$$\int_{\mathcal{X}} \psi_\xi = \int_{\mathcal{X}} \psi_0 = 1.$$

The first assumption in the above theorem means that the equilibrium dynamics has good ergodic properties, while the second one ensures that the perturbation is not too strong. A typical way of proving that $(\mathcal{A}_0^*)^{-1} \mathcal{A}_1^*$ is bounded on $\mathcal{H}$ is to show that $\mathcal{A}_1$ is $\mathcal{A}_0$-bounded: $D(\mathcal{A}_0) \subset D(\mathcal{A}_1)$ and there exists $a, b > 0$ such that $\|\mathcal{A}_1 \varphi\| \leqslant a \|\mathcal{A}_0 \varphi\| + b \|\varphi\|$ for $\varphi \in D(\mathcal{A}_0)$.

The proof of Theorem 3.1 is very simple. We already know that the solution of (3.16) is unique and that (3.17) provides the solution when the series on the right-hand side of (3.17) converges.

This convergence is guaranteed by the convergence in $\mathcal{B}(\mathcal{H})$ of the series

$$\sum_{n=1}^{+\infty}(-\xi)^n \left[(\mathcal{A}_0^*)^{-1}\,\mathcal{A}_1^*\right]^n,$$

which is ensured by the condition $|\xi| r < 1$.

3.1.3.3 Linear response and correlation functions

Linear response properties are first order deviations (in ξ) of average properties computed in the nonequilibrium steady state compared to the same average property computed at equilibrium. Averages in the nonequilibrium steady state are obtained by the integration of an observable h with respect to the measure ψ_ξ:

$$\langle h\rangle_\xi = \int_{\mathcal{X}} h(x)\,\psi_\xi(x)\,dx = \langle h, f_\xi\rangle_{L^2(\psi_0)},$$

while equilibrium averages, denoted by $\langle h\rangle_0$, correspond to an integration with respect to ψ_0. In fact, upon considering $h - \langle h\rangle_0$ instead of h, there is no restriction in studying the linear response of an observable $h \in \mathcal{H}$, for which $\langle h\rangle_0 = 0$ and $\langle h\rangle_\xi = \mathrm{O}(\xi)$.

The appropriate response functions to be averaged, denoted by R in the sequel, are determined by the physics of the problem. For instance, it is the projected velocity (3.8) for the Langevin dynamics with an additional constant forcing term, and the thermal current (3.11) for one dimensional chains coupled to thermostats with different temperatures at the boundaries.

Susceptibilities or transport coefficients are then defined as follows (recall that $R \in \mathcal{H}$):

$$\alpha = \lim_{\xi\to 0} \frac{\langle R\rangle_\xi}{\xi}. \tag{3.18}$$

In practice, an estimate of α can be obtained by choosing a value of ξ sufficiently small, approximating $\langle R\rangle_\xi$ by a longtime average over one realization of the dynamics similar to (2.3), and dividing this quantity by ξ. In order to check that the value of ξ is indeed small enough to neglect higher order contributions, it is possible for instance to check the linearity of the response by computing approximations of $\langle R\rangle_\xi$ with ξ replaced by, say, $\xi/2$ or 2ξ.

Now, using the expression (3.17) of the invariant measure in terms of the perturbation parameter ξ, and the equality

$$-\mathcal{A}_0^{-1} = \int_0^{+\infty} \mathrm{e}^{t\mathcal{A}_0}\,dt$$

as operators on $\mathcal{H}$ (which, to be justified, requires some decay properties of the semi-group), linear response properties can be rephrased using correlation functions. Introducing the function $S = \mathcal{A}_1^*\mathbf{1}$, it holds

$$\alpha = \int_{\mathcal{X}} R\,\mathrm{f}_1\,\psi_0 = -\int_{\mathcal{X}} \left[\mathcal{A}_0^{-1}R\right]\left[\mathcal{A}_1^*\mathbf{1}\right]\,\psi_0 = \int_0^{+\infty} \mathbb{E}\Big(R(x_t)S(x_0)\Big)dt, \tag{3.19}$$

where the expectation is taken over all initial conditions distributed according to $\psi_0(x)\,dx$, and over all realizations of the reference equilibrium dynamics (with generator $\mathcal{A}_0$). The function S may be called a conjugated response. Note that its expression is determined by the applied perturbation $\mathcal{A}_1$, and not by the response function R.

The autocorrelation of R is recovered for perturbations such that $S \propto R$. For the two examples presented in Section 3.1.2, studied in greater detail below, $S(q,p) = \beta R(q,p) = \beta F\cdot M^{-1}p$ for (3.7), while $S(q,p) = \gamma\beta^2(p_1^2 - p_N^2)$ for (3.10). In the latter case, S cannot be related to the response function defined in (3.11).

3.1.3.4 Some examples

We present an application of the general definitions provided in Section 3.1.3.3 to the two prototypical examples introduced in Section 3.1.2. This gives the definition of the mobility of a system described by a Langevin equation, and of the thermal conductivity of one dimensional chains.

Definition of the mobility.

We consider the dynamics (3.7). The linear response of the projected velocity (3.8) allows to define the mobility in terms of the autocorrelation of the projected velocity for a system evolving according to the reference dynamics with generator $\mathcal{A}_0$ defined in (3.13):

$$\alpha = \lim_{\xi \to 0} \frac{\left\langle F \cdot M^{-1} p \right\rangle_\xi}{\xi} = \beta \int_0^{+\infty} \mathbb{E}\Big((F \cdot M^{-1} p_t)(F \cdot M^{-1} p_0) \Big)\, dt. \tag{3.20}$$

In fact, a simple computation also allows to relate the mobility defined by the linear response of a nonequilibrium dynamics, to the self-diffusion coefficient obtained from the longtime behavior of the projected position $F \cdot q_t$ for an *equilibrium* dynamics, in a diffusive scaling. Diffusive properties of Langevin dynamics were studied in [120,133]. The diffusion coefficient is defined by the so-called Einstein formula

$$D = \lim_{T \to +\infty} \frac{\mathbb{E}\Big(F \cdot (q_T - q_0) \Big)^2}{2T},$$

where the expectation is over all initial conditions distributed according to (3.14), and over all realizations of the reference equilibrium dynamics (with generator $\mathcal{A}_0$ defined in (3.13)). The relation between the mobility and the self-diffusion coefficient is

$$\alpha = \beta D.$$

This equality is based on the identity

$$\mathbb{E}\Big(F \cdot (q_T - q_0) \Big)^2 = 2T \int_0^T \mathbb{E}\Big((F \cdot M^{-1} p_t)(F \cdot M^{-1} p_0) \Big) \left(1 - \frac{t}{T} \right) dt.$$

An application of the dominated convergence theorem gives the conclusion when the autocorrelation function is integrable, using the expression (3.20) of the mobility α.

Definition of the thermal conductivity.

We now turn to the dynamics (3.10). The thermal conductivity is defined by the linear response of the energy current :

$$\kappa = \lim_{\Delta T \to 0} \frac{\langle J \rangle_{\Delta T}}{\Delta T} = -\beta^2 \gamma \int_0^{+\infty} \int_{\mathcal{E}} \left(\mathrm{e}^{-t\mathcal{A}_0} J \right) (p_1^2 - p_N^2) \psi_0 \, dt. \tag{3.21}$$

Some (non trivial) manipulations allow to rewrite the above correlation in terms of the energy current autocorrelation (see for instance [15, 100]):

$$\kappa = 2\beta^2 \int_0^{+\infty} \mathbb{E}\Big(j_{i+1,i}(q_t, p_t) J(q_0, p_0) \Big)\, dt = \frac{2\beta^2}{N-1} \int_0^{+\infty} \mathbb{E}\Big(J(q_t, p_t) J(q_0, p_0) \Big)\, dt, \tag{3.22}$$

where the equalities hold for any $i = 1, \ldots, N-1$.

3.1.3.5 Artificial dynamics

Transport coefficients can be computed by specifying both a perturbation (described by its generator $\mathcal{A}_1$) and an appropriate response function R. Once these two quantities are provided, the transport coefficient is obtained by (3.18) or (3.19). In general, the expressions of $\mathcal{A}_1$ and R are motivated by an analogy with experimental setups.

Now, the perturbation $\mathcal{A}_1$ actually enters only through the function $S = \mathcal{A}_1^* \mathbf{1}$. There is therefore some freedom in choosing a perturbation different from the physically relevant one, while ensuring that the linear response is correct since $\mathcal{A}_1^* \mathbf{1}$ is preserved. This is the basis of the "synthetic NEMD" algorithms (with the terminology of [55]), in which non physical perturbations are considered. The interest of these non physical perturbations is that they may have better numerical properties than the standard, physically motivated perturbations: the average linear responses are the same, but the variance of the observables may be different, or the sizes of the transient regime before the steady state is reached may be different.

Two synthetic dynamics can be proposed for thermal transport in one dimensional chains. They perturb the reference dynamics (Hamiltonian dynamics with Langevin thermostats at the same temperature at the boundaries) by nongradient forcing terms, instead of modifying the temperatures at the boundaries. These dynamics are bulk driven (the forcing is felt directly at every site in the chain).

(i) In [54, 56, 103, 110] a non-gradient perturbation $-\xi\Big(v'(q_{i+1} - q_i) + v'(q_i - q_{i-1})\Big)$ is applied at site i, with appropriate modifications at the boundaries:

$$\begin{cases} dq_i = p_i \, dt, \\ dp_i = \Big((1-\xi)v'(q_{i+1} - q_i) - (1+\xi)v'(q_i - q_{i-1})\Big)dt, \qquad i \neq 1, N, \\ dp_1 = \Big((1-\xi)v'(q_2 - q_1) - v'(q_1)\Big)dt - \gamma p_1 \, dt + \sqrt{2\gamma T}\, dW_t^1, \\ dp_N = -(1+\xi)v'(q_N - q_{N-1})\, dt - \gamma p_N \, dt + \sqrt{2\gamma T}\, dW_t^N, \end{cases}$$

The generator of the perturbation of the reference dynamics with generator (3.15) reads

$$\mathcal{A}_1 = -v'(q_2 - q_1)\partial_{p_1} - \sum_{i=2}^{N-1} \Big(v'(q_{i+1} - q_i) + v'(q_i - q_{i-1})\Big)\partial_{p_i} - v'(q_N - q_{N-1})\, \partial_{p_N},$$

so that $\mathcal{A}_1^* = -\mathcal{A}_1 - 2\beta J$.

(ii) Hamiltonian perturbations can also be employed. In this case, the dynamics is the Hamiltonian dynamics associated with the Hamiltonian $H_0 + \xi H_1$ with

$$H_1(q,p) = \sum_{i=1}^{N} i\varepsilon_i(q,p),$$

where ε_i is defined in (3.12), and the two end sites are still coupled to Langevin thermostats at the same temperature T. The generator of the perturbation is

$$\mathcal{A}_1 = \nabla_p H_1 \cdot \nabla_q - \nabla_q H_1 \cdot \nabla_p,$$

so that $\mathcal{A}_1^* = -\mathcal{A}_1 - \beta J$.

In both cases, $S = \mathcal{A}_1^* \mathbf{1} = -c\beta J$ for some constant $c > 0$, so that the linear response of J allows to recover the thermal conductivity, up to a known multiplicative constant (in view of the general result (3.19) and of the definition (3.22) of the thermal conductivity).

3.2 Thermal transport in one dimensional chains

Thermal transport properties are usually investigated using Fourier's law: denoting by T the temperature in the system,

$$c_v(T)\,\partial_t T = \nabla \cdot (\kappa(T)\nabla T), \tag{3.23}$$

where c_v is the heat capacity and κ is the thermal conductivity (a matrix, in general). Fourier's law allows to discuss the relaxation to equilibrium of isolated systems. It expresses a diffusive behavior of the energy. It can also be used to describe nonequilibrium steady states where the system is put in contact with two reservoirs at different temperatures. In this case, there is a net energy flow from the hotter to the colder reservoir. The heat current density j is proportional to the temperature gradient $j = -\kappa(T)\nabla T$, and is such that

$$\nabla \cdot j = 0.$$

In this setting, the diffusive behavior of the energy is hidden in the transient relaxation to the steady state.

Section 3.2.1 discusses the relevant space-time scalings to consider for microscopic systems governed by dynamics such as (3.10) in order to obtain macroscopic evolution equations such as (3.23). Section 3.2.2 then presents some results on the (non)validity of Fourier's law in one dimensional systems, mostly numerical in nature. Finally, Section 3.2.3 summarizes a numerical study on the surprising behavior of a one dimensional system far from the linear response regime.

3.2.1 Space-time scalings for energy transport

Energy transport properties depend on the space-time scale on which the evolution is observed. Before studying the energy transport in a diffusive time-scale where the evolution is followed over long times $N^2 t$ with space renormalized by a factor N^{-1} (this is the relevant scaling for Fourier's law), the system should first be understood in the hyperbolic time-scale, where the system is studied over long times Nt with space renormalized by a factor N^{-1}. Locally, the state of the system should be close to some equilibrium Gibbs measure consistent with the local invariants of the system, such as the energy, the momentum and the volume for Hamiltonian dynamics. In the hyperbolic scaling, a reduced description of the evolution of the microscopic system is given by a system of partial differential equations involving the invariants of the dynamics, known as the hydrodynamic limit (see [96]). The limiting set of equations is often not difficult to obtain formally. To rigorously prove the convergence, the method of choice is the relative entropy method of Yau [156]. Some appropriate ergodicity properties are however required to apply it. It is currently a major open problem to rigorously derive hydrodynamic limits for deterministic systems [18].

The situation is more favorable when the Hamiltonian dynamics is perturbed by appropriate stochastic processes. Together with Cédric Bernardin, we have proved the hydrodynamic limit for a modified Hamiltonian dynamics, where the kinetic energy function and the potential energy function are equal. Our aim was to consider the simplest possible dynamics relevant for thermal transport. In the model we have investigated, momenta and positions play the same role, and a very simple dynamics is obtained, whose equations formally read (for the i-th degree of freedom)

$$d\eta_i = [v'(\eta_{i+1}) - v'(\eta_{i-1})]\,dt.$$

The proof of the hydrodynamic result follows the lines of the proof given in [60]; see [H28,Theorem 1].

Once the behavior of the system is understood in the hyperbolic space-time scaling, it is possible to study the diffusion of the energy on a longer time-scale. If the process has a diffusive behavior consistent with Fourier's law, then the relevant time scale is indeed the diffusive one. However, the energy often "superdiffuses" in one dimensional chains, so that the correct time scaling for

time should rather be $N^\alpha t$ for $1 < \alpha < 2$ instead of $N^2 t$ (see for instance [117] for a review of the cases when such statements can be made mathematically rigorous). Another signature of the anomalous diffusion in one dimensional systems is the fact that the thermal conductivity defined by an appropriate scaling of (3.21) has no thermodynamic limit as the size of the system goes to infinity. These two anomalous behaviors are a sign that Fourier's law may not be valid in one dimensional system; see Section 3.2.2 for a more precise discussion.

3.2.2 Validity of Fourier's law and thermodynamic limit of the conductivity

For usual three dimensional materials, it is observed in numerical simulations that Fourier's law appropriately describes the behavior of the system. In particular, the thermal conductivity does not depend on the system size, and so, it is a well-defined thermodynamical quantity. On the other hand, the validity of Fourier's law is questionable in one dimensional systems. In particular, there is, in many cases, no thermodynamic limit for the thermal conductivity in these models, see Section 3.2.2.1. This is consistent with some experimental results on the length dependence of the thermal conductance of carbon nanotubes [29, 153].

3.2.2.1 Some facts on the thermodynamic limit of the conductivity in one dimensional systems

Define the thermal conductivity for a one-dimensional chain of oscillators of size N as the total energy current (3.11) divided by the temperature gradient $\Delta T/N$, assuming a linear temperature profile (see (3.21) and (3.22)):

$$\kappa_N = \lim_{\Delta T \to 0} \frac{N \langle J \rangle_{\Delta T}}{\Delta T} = 2\beta^2 \frac{N}{N-1} \int_0^{+\infty} \sum_{i=1}^{N-1} \mathbb{E}\Big(j_{2,1}(q_t, p_t) j_{i+1,i}(q_0, p_0) \Big)\, dt. \tag{3.24}$$

The question is whether κ_N has a finite limit as the system size goes to infinity:

$$\exists ? \quad \overline{\kappa} = \lim_{N \to +\infty} \kappa_N < +\infty. \tag{3.25}$$

This issue has been the subject of many theoretical and numerical studies, see the review papers [18, 44, 107]. The limit (3.25) is often studied using numerical experiments (except in very simple analytical cases corresponding to harmonic potentials). The following facts have been established to date, by theoretical or numerical arguments:

(i) for harmonic systems [132] (even in the presence of a harmonic pinning potentials), $\kappa_N = cN$. This is established by an analytical proof showing that the value of J is independent of N. It is also expected that $\kappa_N \sim N$ for integrable systems [158] (for which there are as many invariants of the dynamics as the number of degrees of freedom). A famous example of such a system is the Toda lattice [83, 146], which corresponds to a chain of oscillators with the interaction potential ($b > 0$)

$$v(r) = \frac{\mathrm{e}^{-br} + br - 1}{b^2}.$$

For this potential, it is observed numerically that κ_N is constant.

(ii) the limit (3.25) exists for rotor chains (*i.e.* (3.10) when the interaction potential is $v(r) = 1 - \cos(r)$; see the references in Section 3.2.3), systems with pinning potentials for which the interaction potential and/or the pinning potential is anharmonic, or systems subjected to specific random perturbations for which the momentum of the system is not conserved while energy is (typically, changing the sign of the velocities at random times) [15, 16].

(iii) for chains with "generic" anharmonic potentials (non-integrable systems) and no pinning potentials, the conductivity is observed to diverge as N^α with $0 < \alpha < 1$. The addition of a stochastic perturbation preserving both the total momentum and the energy (such as exchanging the velocities of neighboring atoms) does not change qualitatively the picture. Such perturbations, introduced in [12], aim at modeling the effect of the nonlinearities of the potential, and also ensure that the only invariants of the dynamics are the energy and the total momentum. For harmonic interactions, it can be proved theoretically that $\kappa_N \sim \sqrt{N}$, while for anharmonic interactions $\kappa_N \leqslant C\sqrt{N}$ (see [13]).

(iv) systems with atoms of random masses can be considered as well. For harmonic systems with free boundary conditions [134], the conductivity diverges as $\kappa_N \sim \sqrt{N}$ (this is also what we observed for carbon nanotubes in our numerical study [H16]), while $\kappa_N \sim N^{-1/2}$ for fixed boundary conditions [27] and κ_N decreases exponentially when some harmonic pinning potential is considered. Depending on the boundary conditions, other scaling regimes can be obtained [43]. There are also several studies on the influence of mass disorder on anharmonic chains, such as [45], but the general conclusion is that mass disorder *per se* is not sufficient to prevent the divergence of the thermal conductivity.

A question related to the convergence (3.25) is whether the dynamics of infinite dimensional chains of oscillators is such that the energy current autocorrelation (an appropriate generalization of the integrand in the rightmost term of (3.24)) is an integrable function of time or not. For instance, for the simplified Hamiltonian dynamics studied in [H28], we proved that for harmonic interactions and a stochastic perturbation preserving the invariants of the system, the current autocorrelation function decays as $t^{-1/2}$, so that the thermal conductivity obtained from the Green-Kubo formula (generalizing (3.22) for infinite systems) is infinite, see Theorem 4 in [H28].

3.2.2.2 Numerical studies of stochastically perturbed systems

The scaling of the thermal conductivity for systems subjected to stochastic perturbations preserving both the energy and the momentum (such as [13]) can be rigorously determined for harmonic interactions, while only an upper bound is obtained for anharmonic interactions (see the discussion at the end of item (iii) above). To complement the theoretical results and characterize more precisely the divergence of the thermal conductivity for anharmonic potentials, we have performed extensive sets of numerical computations. In particular we have considered the Toda chains in [H22], and various additional potentials for the simplified Hamiltonian dynamics proposed in [H28].

For Toda chains, we chose the simplest possible stochastic perturbation conserving both momentum and energy: Nearest neighbor particles exchange their momenta at random times distributed according to an exponential law of parameter $\gamma > 0$. We observe that the divergence $\kappa_N \sim N$ is destroyed by the addition of a stochastic perturbation, and transforms into a divergence $\kappa_N \sim N^\alpha$ for $0 < \alpha \leqslant 1/2$. The exponent α depends on the noise intensity γ, in a seemingly monotonically increasing way, which is quite surprising (it is indeed expected that stronger noises lead to less conduction). This may be explained by the fact that the noise destroys some diffusive phenomena due to nonlinearities, like localized breathers, so that the current-current correlation decays slower when more noise is present.

This dependence on the noise intensity is also observed in [H28]. It suggests that any theory claiming the existence of a universal parameter α for the divergence of the thermal conductivity (see the references in [107]) has to be properly circumstanced.

On the other hand, recent theoretical results [14] seem to indicate that, in an infinite one dimensional chain perturbed by a stochastic noise locally preserving energy and momentum, the decay of the current autocorrelation function depends only very mildly on γ. It is not completely clear whether the exponent in the decay of the current autocorrelation function is the same as the one characterizing the divergence of the thermal conductivity in the thermodynamic limit – but

this theoretical result definitively calls for additional numerical works studying the dependence of thermal properties with γ.

3.2.3 Nonlinear response under a strong mechanical forcing

The previous sections dealt with properties of the system in the linear response regime. We consider in this section a system far from the linear response regime, and subjected to two forcings: a (weak) thermal forcing and a (strong) mechanical one. We are not aware of any previous numerical study of energy transport in mechanically forced atom chains. The aim is to study the interplay between the thermal and the mechanical forcings. This presentation is based on [H24].

We consider a chain of N rotors. The name "rotor" is motivated by the fact that the configuration of a particle is described by an angle q and an angular velocity p, while the interaction potential between neighboring particles is $v(q) = 1 - \cos(q)$. The leftmost rotor is attached to a wall and put in contact with a Langevin thermostat at temperature T_{L}, while the rightmost rotor is subjected to a constant external force F and put in contact with another Langevin thermostat at temperature T_{R}. We consider a system with free boundary conditions on the right end (fixed boundary conditions give very similar results), the evolution equations of which read:

$$\begin{cases} dq_i = p_i\,dt, \\ dp_i = \Big(\sin(q_{i+1}-q_i) - \sin(q_i - q_{i-1})\Big)dt, & i \neq 1, N, \\ dp_1 = \Big(\sin(q_2 - q_1) - \sin(q_1)\Big)dt - \gamma p_1\,dt + \sqrt{2\gamma T_{\mathrm{L}}}\,dW_t^1, \\ dp_N = \Big(F - \sin(q_N - q_{N-1})\Big)dt - \gamma p_N\,dt + \sqrt{2\gamma T_{\mathrm{R}}}\,dW_t^N, \end{cases} \tag{3.26}$$

where W_t^1 and W_t^N are independent standard Wiener processes, and $\gamma > 0$ determines the strength of the coupling to the thermostat. In the sequel, we work with $\gamma = 1$. Note that the external constant force F is non-gradient since it does not derive from a periodic potential.

To our knowledge, there is currently no mathematical result ensuring the existence and uniqueness of a smooth invariant measure for (3.26), even in the case $F = 0$. Indeed, the standard techniques used to prove existence and uniqueness of an invariant measure for chains of oscillators under thermal forcing (see for instance [25, 129]) do not apply here. In particular, there is no mechanism to prevent energy from concentrating in the center of the chain. However, we have not observed such problems in our numerical simulations.

Our numerical results indicate that a steady state is reached. If $F = 0$ and $T_{\mathrm{L}} = T_{\mathrm{R}} = T$, the system is in equilibrium, and the Gibbs measure at temperature T is an invariant probability measure. When $T_{\mathrm{L}} \neq T_{\mathrm{R}}$ with $F = 0$, the properties of the non-equilibrium stationary state have been studied numerically by various authors [63–65,155]. If $F \neq 0$, the system is out-of-equilibrium even if $T_{\mathrm{L}} = T_{\mathrm{R}}$. The force, in the stationary state, induces an energy current towards the left. The stationary state cannot be computed explicitly and, if F is large, linear response theory cannot be used to obtain information about the conductivity of the system. If $T_{\mathrm{L}} \neq T_{\mathrm{R}}$ and $F \neq 0$, there are two mechanisms that separately generate an energy current in the system: The mechanical force F and the thermal force given by the temperature gradient. It is however difficult to separate the contributions of each mechanism. The numerical experiments reported in [H24] show that these two mechanisms are not necessarily additive. In particular, even when the two forcings generate a current in the same direction, one mechanism may reduce the effect of the other one, leading to counterintuitive results.

Details on the numerical integration of the dynamics are given in [H24]. Figure 3.1 shows plots of the average velocities, kinetic and potential temperatures for different system sizes. The potential temperature is obtained by inverting the function which, to a given temperature, associates the canonical average of the potential energy. Note that the temperature is maximal in the center of

the system, whereas, in systems where there is no mechanical force, the temperature decreases monotonically from the hot end to the cold one. We also checked in [H24] by various statistical tests that, for sufficiently long systems, a local Gibbs equilibrium parameterized by the average velocity and the (kinetic or potential) temperature holds.

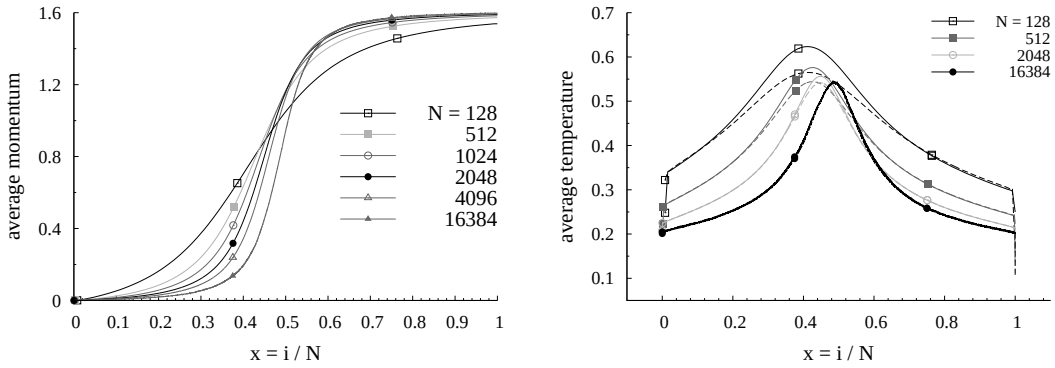


Fig. 3.1. Rescaled profiles for systems of increasing size $N = 2^k$. The x variable is the site index i divided by N. The value of the nongradient force is $F = 1.6$ and $T_{\mathrm{L}} = T_{\mathrm{R}} = 0.2$. Left: momenta. Right: kinetic (solid lines) and potential (dashed lines) temperatures.

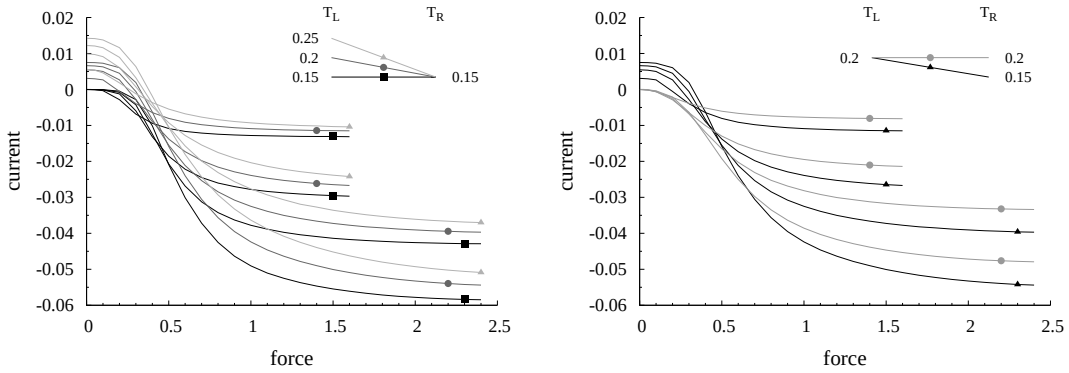


Fig. 3.2. Comparison of the currents with fixed temperature on the right end and increasing temperatures on the left end. From top to bottom: decreasing system sizes $N = 2048, 512, 256, 128$ (the ordering is the same for all situations considered; for the longest systems, we have considered forces $0 \leqslant F \leqslant 1.6$; for the shortest ones, we have considered the range $0 \leqslant F \leqslant 2.4$).

For large mechanical forcings F (see Figure 3.2), we observe numerically that

(a) when T_{R} is fixed (Figure 3.2, left), the current varies qualitatively as when there is no mechanical forcing: The absolute value of the current increases when T_{L} decreases. In this case, a positive thermal conductivity is observed (for a fixed value F of the mechanical forcing, considering only the response in the limit when $T_{\mathrm{R}} - T_{\mathrm{L}} \to 0$).

(b) when T_{L} is fixed (Figure 3.2, right), the current has a surprising behavior: Its absolute value increases when T_{R} decreases. This means that the thermal forcing, which is naively expected to reduce the current induced by the mechanical forcing, actually enhances it. In this case, a negative thermal conductivity is observed (again, for a fixed value F of the mechanical forcing).

We have no satisfactory explanation for this surprising behavior at the moment, although some physical conjectures are provided in [H24].

3.3 Shear viscosity: A mathematical study of a bulk driven nonequilibrium dynamics

Many mathematical works studied the definition and the properties of the self-diffusion coefficient (see for instance the recent contributions [76, 77, 121] and references therein), or the thermal conductivity of one dimensional chains (see the references in Section 3.2). On the other hand, the mathematical literature on the atomistic definition and the properties of the shear viscosity is rather scarce in comparison with the numerous works in computational physics. This motivated us to study numerical methods to compute the shear viscosity in [H26].

The shear viscosity characterizes the resistance of a fluid to flow when subjected to a shear stress. For Newtonian fluids, it is the tensor linearly relating the shear stress to the velocity gradient (see (3.36) below). A review of the most standard approaches in molecular simulation to compute the shear viscosity can be read in [55, 147]. A popular method is to use a version of the SLLOD algorithm (see the references in [35]), in which an external non-Hamiltonian forcing term is added both to the positions and the momenta. This method is used in conjunction with Lees-Edwards boundary conditions [102], which are boundary conditions consistent with a constant shear rate and a linear velocity profile. However, a mathematical study of the linear response in this framework is cumbersome since the boundary conditions for the associated Fokker-Planck operators are time-dependent and also depend on the shear rate. It is easier to study techniques relying on periodic non-gradient forcings. In this case, standard periodic boundary conditions can be used. This is the path we follow here.

We decided to use a standard Langevin dynamics as the underlying dynamics of the system since this dynamics is ergodic and has many nice mathematical properties, while still being sufficiently close to the Hamiltonian dynamics. We are able to rigorously prove linear response results using recent developments on hypocoercivity [150], and also obtain an effective equation on the observed velocity profile in terms of the applied external force through some closure relation. One of our main concerns is the dependence of the viscosity as a function of the parameters of the underlying dynamics, in particular the friction. We analyzed the large friction asymptotics by extending and adapting mathematical studies of the properties of the self-diffusion coefficient [76, 77, 121].

This section is organized as follows. The dynamics we use is presented in Section 3.3.1. The shear viscosity is then defined in Section 3.3.2 (see in particular Section 3.3.2.2), and its behavior as a function of the Langevin friction is studied there as well. Finally, some numerical results illustrate the theoretical results in Section 3.3.3.

3.3.1 Description of the dynamics

We consider a system of N particles, enclosed in a periodic simulation box $\mathcal{D}$. For simplicity of notation, we restrict ourselves to two-dimensional systems, so that $\mathcal{D} = L_x\mathbb{T}\times L_y\mathbb{T}$. The particles are described by their positions $q = (q_1, \dots, q_N) \in \mathcal{D}^N$ and their momenta $p = (p_1, \dots, p_N) \in \mathbb{R}^{2N}$, and we assume that they have identical masses $m > 0$. Our results can however straightforwardly be extended to the general case of particles with different masses and/or three-dimensional systems. We write $q_i = (q_{xi}, q_{yi}) \in \mathcal{D}$, $p_i = (p_{xi}, p_{yi}) \in \mathbb{R}^2$, as well as $q_x = (q_{x1}, \dots, q_{xN})$, $p_x = (p_{x1}, \dots, p_{xN})$ and similar definitions for q_y, p_y. The mass density of the system is $\rho = mN/|\mathcal{D}|$, $|\mathcal{D}| = L_xL_y$ being the volume of the box. As usual, we denote by

$$H(q,p) = \sum_{i=1}^{N} \frac{p_i^2}{2m} + V(q)$$

the Hamiltonian of the system, the function V being the potential energy.

3.3.1.1 Nonequilibrium Langevin dynamics

The equations of motion we consider are a linear perturbation of the Langevin equations, with some additional non-gradient external force in the x-direction (the direction of the flow), the magnitude of the force depending only on the y coordinate of the particle. The non-gradient term mimicks the effect of some shear stress, and hence allows to create a velocity profile in the direction of the forcing, from which the viscosity of the fluid can be extracted. The dynamics reads (for $i = 1, \dots, N$):

$$\begin{cases} dq_{i,t} = \dfrac{p_{i,t}}{m}\, dt, \\ dp_{xi,t} = -\nabla_{q_{xi}} V(q_t)\, dt + \xi F(q_{yi,t})\, dt - \gamma_x \dfrac{p_{xi,t}}{m}\, dt + \sqrt{\dfrac{2\gamma_x}{\beta}}\, dW_t^{xi}, \\ dp_{yi,t} = -\nabla_{q_{yi}} V(q_t)\, dt - \gamma_y \dfrac{p_{yi,t}}{m}\, dt + \sqrt{\dfrac{2\gamma_y}{\beta}}\, dW_t^{yi}, \end{cases} \tag{3.27}$$

where $\beta = 1/(k_{\mathrm{B}}T)$ is the inverse temperature, ξ is the magnitude of the external nongradient force, $(W_t^x, W_t^y)_{t\geq 0}$ is a $2N$-dimensional standard Brownian motion and the friction coefficients γ_x, γ_y are real positive numbers. In order to avoid irrelevant technical issues, we assume in the sequel that the potential V and the external force F belong respectively to $C^\infty(\mathcal{D}^N)$ and $C^\infty(L_y\mathbb{T})$.

The infinitesimal generator of the equilibrium Langevin process (*i.e.* (3.27) in the case when $\xi = 0$), reads $\mathcal{A}_0 = \mathcal{A}_{\mathrm{ham}} + \mathcal{A}_{\mathrm{thm}}$, with

$$\mathcal{A}_{\mathrm{ham}} = \frac{p}{m} \cdot \nabla_q - \nabla V(q) \cdot \nabla_p, \qquad \mathcal{A}_{\mathrm{thm}} = \sum_{\alpha = x,y} \gamma_\alpha \left(-\frac{p_\alpha}{m} \cdot \nabla_{p_\alpha} + \frac{1}{\beta} \Delta_{p_\alpha} \right).$$

Note that the canonical measure

$$\psi_0(q,p)\, dq\, dp = Z^{-1}\, \mathrm{e}^{-\beta H(q,p)}\, dq\, dp \tag{3.28}$$

is invariant by the dynamics (3.27) when $\xi = 0$, and is actually the only invariant measure (see [H26, Theorem 1]). The adjoint operator on $L^2(\psi_0)$ of the generator is $\mathcal{A}_0^* = -\mathcal{A}_{\mathrm{ham}} + \mathcal{A}_{\mathrm{thm}}$. The generator of the nonequilibrium perturbation and its adjoint on $L^2(\psi_0)$ respectively read

$$\mathcal{A}_1 = \sum_{i=1}^N F(q_{yi}) \partial_{p_{xi}}, \qquad \mathcal{A}_1^* = -\sum_{i=1}^N F(q_{yi}) \partial_{p_{xi}} + \frac{\beta}{m} p_{xi} F(q_{yi}).$$

The generator of the dynamics (3.27) is therefore $\mathcal{A}_\xi = \mathcal{A}_0 + \xi \mathcal{A}_1$.

3.3.1.2 Existence and uniqueness of an invariant measure

When $\xi \neq 0$, there is no obvious invariant probability measure for (3.27), and the very existence of such a measure is not guaranteed *a priori*. However, in the case when $\gamma_x, \gamma_y > 0$, standard techniques based on Lyapunov functions and hypoellipticity arguments can be used to prove the existence and uniqueness of an invariant measure that has a smooth density with respect to the Lebesgue measure.

Theorem 3.2. *Consider $\gamma_x, \gamma_y > 0$ and suppose that V, F are smooth. Then, for any $\xi \in \mathbb{R}$, the dynamics* (3.27) *has a unique smooth invariant probability measure with density $\psi_\xi \in C^\infty(\mathcal{D}^N \times \mathbb{R}^{2N})$. In addition, there exists $\xi^* > 0$ such that, for any $\xi \in (-\xi^*, \xi^*)$, the following expansion holds in $L^2(\psi_0)$:*

$$\psi_\xi = f_\xi \psi_0, \qquad f_\xi = 1 + \sum_{k\geq 1} \xi^k \mathrm{f}_k, \tag{3.29}$$

where $\mathrm{f}_k \in \mathcal{H} = \{\mathbf{1}\}^\perp$ *is such that* $\|\mathrm{f}_k\|_{L^2(\psi_0)} \leqslant C(\xi^*)^{-k}$ *for some constant* $C > 0$ *independent of* ξ.

The existence and uniqueness of an invariant measure in the case when either $\gamma_x = 0$ or $\gamma_y = 0$ is a much more difficult question.

Let us briefly sketch the proof of Theorem 3.2. The existence and the uniqueness of an invariant measure that has a smooth density with respect to the Lebesgue measure for any $\xi \in \mathbb{R}$ is a standard result since the position space is compact and the forces are smooth. It suffices to use hypoellipticity arguments and take the kinetic energy as a Lyapunov function (see for instance [128] for the general strategy, and [121, Appendix A] for the specific case under consideration). To obtain the expression of this invariant measure as an expansion in the parameter ξ, we follow the lines of the general argument sketched in Section 3.1. Standard hypocoercivity results show that $\mathcal{A}_0^{-1}$ is bounded on $\mathcal{H}$ (and in fact compact by a treatment similar to [76, 77, 118]). Moreover, a simple computation shows that there exists a constant $C > 0$ such that, for any smooth test function φ,

$$\|\mathcal{A}_1\varphi\|^2_{L^2(\psi_0)} \leqslant C \left| \langle \varphi, \mathcal{A}_0\varphi \rangle_{L^2(\psi_0)} \right| \leqslant C \|\varphi\|_{L^2(\psi_0)} \, \|\mathcal{A}_0\varphi\|_{L^2(\psi_0)}.$$

so that, for any $\varphi \in \mathcal{H}$,

$$\|\mathcal{A}_1\mathcal{A}_0^{-1}\varphi\|^2_{L^2(\psi_0)} \leqslant C \|\mathcal{A}_0^{-1}\varphi\|_{L^2(\psi_0)} \, \|\varphi\|_{L^2(\psi_0)}.$$

Since $\mathrm{Ran}(\mathcal{A}_1) \subset \mathcal{H}$, this shows that $\mathcal{A}_1\mathcal{A}_0^{-1}$ is a bounded operator on $\mathcal{H}$. The same holds true for $(\mathcal{A}_0^*)^{-1}\mathcal{A}_1^*|_{\mathcal{H}}$, which is its adjoint on $\mathcal{H} \subset L^2(\psi_0)$.

3.3.2 Mathematical analysis of the viscosity

The nonequilibrium perturbation is such that

$$-\mathcal{A}_1^*\mathbf{1} = -\frac{\beta}{m} \sum_{i=1}^N p_{xi} F(q_{yi}).$$

In view of Theorem 3.2, and relying on the argument presented in Section 3.1.3, it easy to prove the following linear response result.

Corollary 3.1. *Under the same assumptions as in Theorem 3.2, and for any sufficiently regular function* h,

$$\lim_{\xi\to 0} \frac{\langle \mathcal{A}_0 h \rangle_\xi}{\xi} = -\frac{\beta}{m} \left\langle h, \sum_{i=1}^N p_{xi} F(q_{yi}) \right\rangle_{L^2(\psi_0)}. \tag{3.30}$$

Moreover, for any function $h \in \mathcal{H}$,

$$\lim_{\xi\to 0} \frac{\langle h \rangle_\xi}{\xi} = -\frac{\beta}{m} \left\langle \mathcal{A}_0^{-1} h, \sum_{i=1}^N p_{xi} F(q_{yi}) \right\rangle_{L^2(\psi_0)}. \tag{3.31}$$

In the next sections, our aim is to understand the behavior of the average velocity profile of the fluid as a function of the applied force F.

3.3.2.1 Local conservation of the longitudinal velocity.

We prove in this section a conservation equation for velocities in the x-direction, when spatial averages over small windows in the transverse direction y are considered. This allows to state an

equation relating the off-diagonal terms of the stress tensor and the nongradient force acting on the system, see (3.35) below. Our derivation may be seen as a mathematically rigorous rewriting of the seminal work of Irving and Kirkwood [91]. We henceforth assume that the potential energy is given by a sum of pairwise interactions:

$$V(q_1, \dots, q_N) = \sum_{1 \leqslant i < j \leqslant N} \mathcal{V}(|q_i - q_j|), \tag{3.32}$$

for some given smooth potential $\mathcal{V}$.

Consider the following average longitudinal velocity:

$$U_x^\varepsilon(Y, q, p) = \frac{L_y}{Nm} \sum_{i=1}^N p_{xi} \chi_\varepsilon (q_{yi} - Y), \tag{3.33}$$

where χ_ε (with $0 < \varepsilon \leqslant 1$) is an approximation of the identity on $L_y\mathbb{T}$. The factor L_y in (3.33) accounts for the fact that χ_ε has units of inverse lengths: in fact,

$$\frac{1}{L_y} \int_0^{L_y} U_x^\varepsilon(Y, q, p)\, dY = \frac{1}{Nm} \sum_{i=1}^N p_{xi}$$

is the average velocity of the system. In practice, averages such as (3.33) are computed with bin indicator functions.

We also need a spatially localized (with respect to the altitude Y) version of the off-diagonal term of the stress tensor. This quantity is given by the following expression:

$$\Sigma_{xy}^\varepsilon(Y, q, p) = \frac{1}{L_x} \left(\sum_{i=1}^N \frac{p_{xi} p_{yi}}{m} \chi_\varepsilon (q_{yi} - Y) - \sum_{1 \leqslant i < j \leqslant N} \mathcal{V}'(|q_i - q_j|) \frac{q_{xi} - q_{xj}}{|q_i - q_j|} \int_{q_{yj}}^{q_{yi}} \chi_\varepsilon(s - Y)\, ds \right). \tag{3.34}$$

The fact that it can be interpreted as some stress tensor is motivated by the conservation law (3.35). Besides, the spatial average over Y of $\Sigma_{xy}^\varepsilon(Y, q, p)$ is the standard expression for the off-diagonal term of the pressure tensor. The expression (3.34) comes out naturally from the mathematical analysis (see the proof of Proposition 3.1 in [H26]), and was already proposed in [148].

The relationship between the local longitudinal velocity and the off-diagonal term of the stress tensor is made precise in the following proposition.

Proposition 3.1. *The limits*

$$u_x(Y) = \lim_{\varepsilon \to 0} \lim_{\xi \to 0} \frac{\langle U_x^\varepsilon(Y, \cdot) \rangle_\xi}{\xi}, \qquad \sigma_{xy}(Y) = \lim_{\varepsilon \to 0} \lim_{\xi \to 0} \frac{\left\langle \Sigma_{xy}^\varepsilon(Y, \cdot) \right\rangle_\xi}{\xi}$$

belong to $C^\infty(L_y\mathbb{T})$ *and*

$$\frac{d\sigma_{xy}(Y)}{dY} + \gamma_x \overline{\rho} u_x(Y) = \overline{\rho} F(Y), \tag{3.35}$$

where $\overline{\rho} = \rho/m$ *is the particle density.*

The proof is based on an application of Corollary 3.1 with (3.33) as a test function. The order of the limits $\varepsilon \to 0$ and $\xi \to 0$ cannot be inverted since the linear response result of Corollary 3.1 cannot be applied with h replaced by the limit of χ_ε (which is a Dirac mass).

3.3.2.2 Closure relation and definition of the viscosity

We now discuss a closure relation for (3.35), which allows to obtain an equation on the average velocity only, from which the viscosity can be extracted. By analogy with continuum fluid mechanics,

we *define* the shear viscosity η as follows:

$$\sigma_{xy}(Y) = -\eta(Y)\frac{du_x(Y)}{dY}. \tag{3.36}$$

This definition leads to the following equation on u_x:

$$-\frac{d}{dY}\left(\eta(Y)\,\frac{du_x(Y)}{dY}\right) + \gamma_x\overline{\rho}u_x(Y) = \overline{\rho}F(Y).$$

In the bulk of homogeneous fluids, the simplest closure is to assume that

$$\eta(Y) = \eta > 0, \tag{3.37}$$

so that the following equation on u_x is obtained:

$$-\eta u_x''(Y) + \gamma_x\overline{\rho}u_x(Y) = \overline{\rho}F(Y). \tag{3.38}$$

In order to ensure the uniqueness of the solution when $\gamma_x = 0$, an additional condition on u_x should be added (such as a vanishing integral over the domain $L_y\mathbb{T}$).

The equation (3.38) obtained with the help of the closure relation is the basis for numerical methods to compute the shear viscosity given a potential energy function V. We were not able to justify mathematically the assumption (3.37), and therefore rely on the numerical validations presented in Section 3.3.3, where we compare numerical profiles of σ_{xy} and $-\eta u_x'$.

3.3.2.3 Dependence of the viscosity on the friction parameter

An important issue is the dependence of the viscosity on the parameters of the dynamics. For the Langevin dynamics (3.27), this means understanding the dependence of the viscosity on the friction parameters γ_x, γ_y. The limits $\gamma_x \to 0$ or $\gamma_y \to 0$ are very difficult to study mathematically without strong assumptions on the potential and/or the geometry of the system. We therefore rely on numerical simulations for these cases (see [H26]). As expected, the viscosity has a finite limit when only one of the friction parameters vanishes.

On the other hand, the limit when one of the friction parameters goes to infinity can be studied mathematically. To this end, we have to understand the limit of the velocity field u_x as either γ_x or γ_y goes to infinity. This is done by rigorous asymptotic analysis. Thanks to (3.38), limiting behaviors of the viscosity may be inferred from the limiting behaviors of the velocity profiles. The key result to obtain the limiting velocity profile is to characterize the limit of some averages with respect to specific solutions of the Poisson equation (see (3.39) below).

In the case $\gamma_y \to +\infty$ for a fixed value $\gamma_x > 0$ for instance (see [H26] for the case $\gamma_x \to +\infty$ with a fixed value of γ_y), we can prove the following result.

Theorem 3.3 (Infinite transverse friction). *Consider a given smooth function G and a longitudinal friction $\gamma_x > 0$. Define $\mathcal{A}_0(\gamma_y) = \mathcal{A}_{\rm ham} + \gamma_x\mathcal{A}_{x,\rm thm} + \gamma_y\mathcal{A}_{y,\rm thm}$, with $\mathcal{A}_{\alpha,\rm thm} = -m^{-1}p_\alpha\cdot\nabla_{p_\alpha} + \beta^{-1}\Delta_{p_\alpha}$, and denote by f_{γ_y} the unique solution in $\mathcal{H}$ of the equation*

$$-\mathcal{A}_0(\gamma_y)f_{\gamma_y} = \sum_{i=1}^{N} p_{xi}G(q_{yi}). \tag{3.39}$$

Then, there exist $f^0 \in H^1(\psi_0)$ and a constant $C > 0$ such that, for all $\gamma_y \geq \gamma_x$,

$$\left\|f_{\gamma_y} - f^0\right\|_{H^1(\psi_0)} \leqslant \frac{C}{\gamma_y}. \tag{3.40}$$

Besides, the function f^0 is of the general form $f^0(q,p) = \sum_{i=1}^{N} G(q_{yi})\phi_i(q_x, q_y, p_x)$, with $\phi_i \in C^\infty$.

The proof is standard: we first write formally an expansion of the velocity in inverse powers of the friction parameters, obtain the equations defining the higher order terms in the expansion, and determine these terms by the solvability conditions of the associated equations (through a Fredholm alternative). The formal computations are then made rigorous thanks to uniform hypocoercivity estimates.

The above result can be used to understand the limit of $u_x(Y)$ as $\gamma_y \to +\infty$. Indeed, by Proposition 3.1,

$$u_x^\varepsilon(Y) = \lim_{\xi\to 0} \frac{\langle U_x^\varepsilon(Y,\cdot)\rangle_\xi}{\xi} = \frac{\beta}{m}\left\langle \mathscr{U}_{\gamma_y}^\varepsilon(Y,q,p), \sum_{i=1}^{N} p_{xi}F(q_{yi})\right\rangle_{L^2(\psi_0)},$$

where $-\mathcal{A}_0(\gamma_y)\mathscr{U}_{\gamma_y}^\varepsilon(Y,\cdot) = U_x^\varepsilon(Y,\cdot)$ is a Poisson equation of the form (3.39) (with $G(y)$ proportional to $\chi_\varepsilon(y-Y)$). The convergence result (3.40) shows that $\mathscr{U}_{\gamma_y}^\varepsilon(Y,\cdot)$ has a limit as $\gamma_y \to +\infty$, and the limiting velocity field reads

$$u_x^{\infty,\varepsilon}(Y) = \frac{\beta L_y}{Nm^2}\left\langle \sum_{j=1}^{N} \chi_\varepsilon(q_{yj}-Y)\phi_j(q_x,q_y,p_x), \sum_{i=1}^{N} p_{xi}F(q_{yi})\right\rangle_{L^2(\psi_0)}.$$

The latter quantity has a limit as $\varepsilon \to 0$. Therefore, the viscosity extracted from (3.38) also has a finite limit. These theoretical considerations are illustrated by numerical simulations in [H26].

3.3.3 Numerical results for the Lennard-Jones fluid

We conclude this section by presenting a few numerical results validating the closure assumption (3.37). Additional numerical results, including a careful study of the dependence of the viscosity on the friction parameters of the Langevin dynamics, can be found in [H26]. The computations are performed for a 2-dimensional Lennard-Jones fluid (with a smoothly truncated potential), and the results are presented in reduced units. The thermodynamic state of the system is determined by the temperature and the density: $\beta = 0.4$, $\rho = 0.69$. We consider $L_x = 360$ and $L_y = 18$, so that the number of simulated particles is $N = 4500$. The remaining adjustable parameters of the model are the force amplitude ξ and the friction parameters γ_x, γ_y. The dynamics (3.27) is integrated using a standard splitting strategy, and average values of the profiles as a function of the altitude y are computed with a binning procedure.

Estimation of the shear viscosity.

The shear viscosity is obtained from a Fourier analysis of (3.38). More precisely, consider the Fourier coefficients

$$U_k = \frac{1}{L_y}\int_0^{L_y} u_x(y)\exp\left(\frac{2\mathrm{i}k\pi y}{L_y}\right)dy, \qquad F_k = \frac{1}{L_y}\int_0^{L_y} F(y)\exp\left(\frac{2\mathrm{i}k\pi y}{L_y}\right)dy.$$

The coefficients U_k can be estimated numerically using averages over a trajectory $(q^n)_{1\leqslant n\leqslant N_{\mathrm{iter}}}$ as

$$U_k^{N_{\mathrm{iter}}} = \frac{1}{N_{\mathrm{iter}}\xi N}\sum_{n=1}^{N_{\mathrm{iter}}}\sum_{j=1}^{N}\frac{p_{xj}^n}{m}\exp\left(\frac{2\mathrm{i}k\pi q_{yj}^n}{L_y}\right),$$

while F_k can be computed analytically for the forces we have considered (see below). The viscosity is then obtained as

$$\eta = \overline{\rho}\left(\frac{F_k}{U_k^{N_{\rm iter}}} - \gamma_x\right)\left(\frac{L_y}{2k\pi}\right)^2. \tag{3.41}$$

This equality is valid for any $k \in \mathbb{Z}\backslash\{0\}$. However, the coefficients U_k decrease very rapidly as $|k|$ increases, so that the relative statistical errors in their estimation increase rapidly. We therefore restricted ourselves to $|k| = 1$ in our numerical simulations.

Nongradient forces.

We consider three different external perturbations, which are all normalized so that $-1 \leqslant F(y) \leqslant 1$:

(i) sinusoidal perturbation: $F(y) = \sin\left(\dfrac{2\pi y}{L_y}\right)$;

(ii) piecewise linear perturbation: $F(y) = \begin{cases} \dfrac{4}{L_y}\left(y - \dfrac{L_y}{4}\right), & 0 \leqslant y \leqslant \dfrac{L_y}{2}, \\ \dfrac{4}{L_y}\left(\dfrac{3L_y}{4} - y\right), & \dfrac{L_y}{2} \leqslant y \leqslant L_y; \end{cases}$

(iii) piecewise constant constant perturbation: $F(y) = \begin{cases} 1, & 0 < y < \dfrac{L_y}{2}, \\ -1, & \dfrac{L_y}{2} < y < L_y. \end{cases}$

Note that only the sinusoidal force satisfies the smoothness assumptions required to derive our results. This shape of perturbation, introduced in [67], is the most popular choice for shear viscosity computations.

Validation of the closure

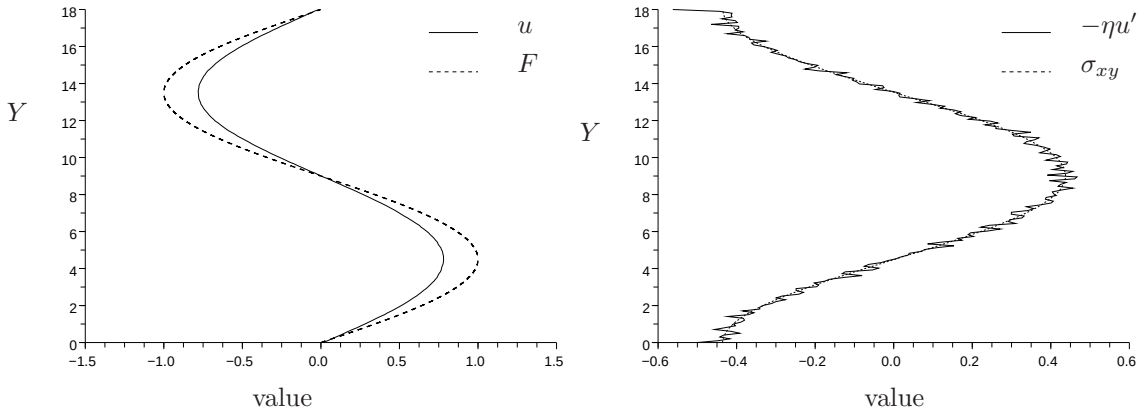


Fig. 3.3. Velocity profile and off diagonal component of the stress tensor for the sinusoidal nongradient force.

We present in Figures 3.3, 3.4 and 3.5 the numerical approximations of the longitudinal velocity u_x and the off-diagonal term of the stress tensor σ_{xy}. The latter function is compared to the quantity $-\eta u_x'$, where u_x' is evaluated from the velocity profile using a second order finite difference scheme. The good agreement between σ_{xy} and $-\eta u_x'$ validates the assumption (3.37), the discrepancies resulting from statistical fluctuations magnified by the numerical derivative, and also, for the piecewise constant force, from the singularity at $L_y/2$.

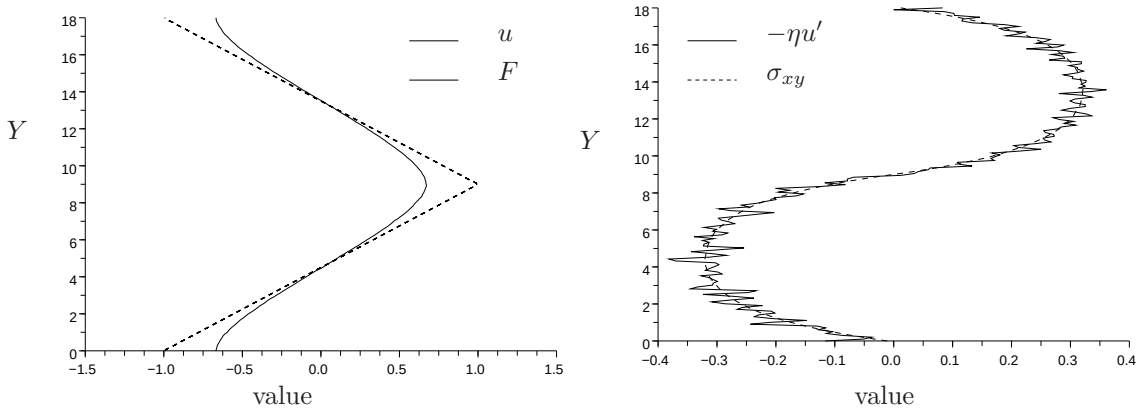


Fig. 3.4. Velocity profile and off diagonal component of the stress tensor for the piecewise linear nongradient force.

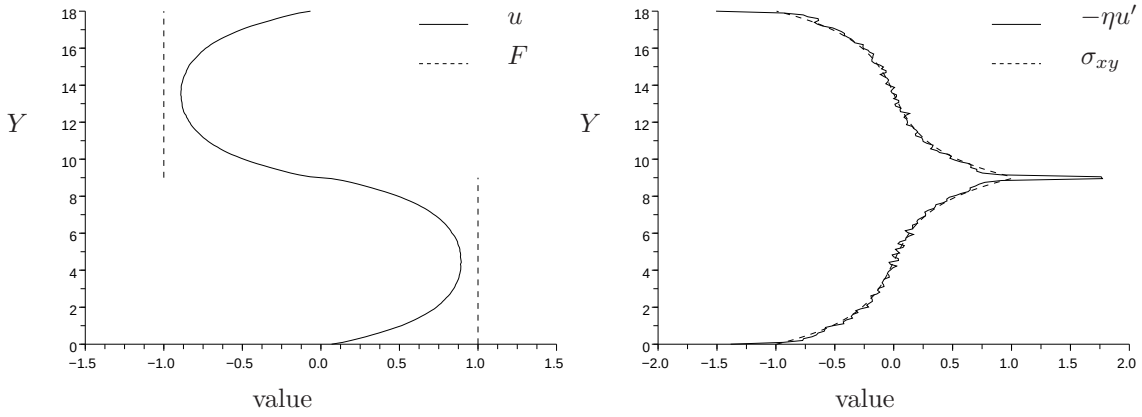


Fig. 3.5. Velocity profile and off diagonal component of the stress tensor for the piecewise constant force.

Besides, the velocity profile is consistent with (3.38), as can be checked by comparing the numerical solution and the solution of (3.38) computed with the value of η estimated from the simulation using (3.41) with $k = 1$.

4

Time-dependent problems in quantum physics

We present in this chapter two works on time-dependent dynamics in quantum physics. A general introduction to some aspects of quantum physics is provided in Sections 4.1.1 and 4.2.1 (following the lines of our proceeding [C4]). In the first study (Section 4.1), the time dependence is actually artificial since the dynamics is a fictitious one allowing to switch from a degenerate eigenstate of some reference Hamiltonian to an eigenstate of a perturbed Hamiltonian. For the time evolution of electronic defects in perfect crystals presented in Section 4.2, there is on the other hand a genuine time dependence arising both from some time dependent external forcing and from the nonlinear dynamics of the defect.

4.1 Adiabatic switching of degenerate eigenstates

This section starts by presenting some elements on the spectral theory of N-body Schrödinger operators (Section 4.1.1), for systems with interacting electrons (Section 4.1.1.1) and also for simpler but non-physical systems with non-interacting electrons (Section 4.1.1.2). The idea is that the eigenstates of non-interacting systems are considered as reference states for which the interaction is turned on progressively in order to transform them into eigenstates of the system with full interactions. This procedure, known as adiabatic switching, is presented in Section 4.1.2 in the simple case when the initial state of the non-interacting system is an eigenstate associated with an isolated, non-degenerate eigenvalue. Section 4.1.3 then presents our contributions to this field [H14, H20, H19]: we show how to perform the adiabatic switching when the eigenstate of the non-interacting system belongs to a degenerate eigenstate. An application of adiabatic switching, the definition of Green's functions and correlation functions for interacting systems using states of non-interacting systems, is finally provided in Section 4.1.4.

4.1.1 Some elements of quantum physics

4.1.1.1 The N-body Schrödinger model

Consider a molecular system with M nuclei of charges $z_1, \dots, z_M$. We omit the spin variable in this presentation, and state the models in atomic units where

$$\hbar = 1, \qquad m_{\mathrm{e}} = 1, \qquad e = 1, \qquad \frac{1}{4\pi\varepsilon_0} = 1,$$

so that z_m is a positive integer. Within the Born-Oppenheimer approximation, the nuclei are modelled as classical point-like particles. This approximation results from a combination of an adiabatic limit (the small parameter being the ratio between the mass of the electron and the mass of the lightest nucleus present in the system), and a semi-classical limit. We refer to [2,3,119,144] and references therein for the mathematical aspects of this approximation.

If the M nuclei are located at points $R_1, \dots, R_M$ of $\mathbb{R}^3$, the nuclear charge distribution and the Coulomb potential generated by this distribution respectively read

$$\rho^{\mathrm{nuc}} = \sum_{m=1}^{M} z_m \delta_{R_m}, \qquad V^{\mathrm{nuc}}(x) = -\sum_{m=1}^{M} \frac{z_m}{|x - R_m|}$$

where δ_{R_m} is the Dirac measure at point R_m. In order to avoid some technical difficulties due to the singularity of the potential generated by point-like nuclei, the nuclear charge distribution is sometimes replaced by the charge distribution of smeared nuclei

$$\rho^{\mathrm{nuc}}(x) = \sum_{m=1}^{M} z_m \chi(x - R_m),$$

where χ is a smooth approximation of the Dirac measure δ_0, or more precisely a non-negative smooth radial function such that $\int_{\mathbb{R}^3} \chi = 1$, supported in a small ball centered at 0. The associated Coulomb potential is then $V^{\mathrm{nuc}}(x) = -(\rho^{\mathrm{nuc}} \star |\cdot|^{-1})(x)$.

Any (pure) state of a system of N electrons is entirely described by a wavefunction $\Psi \in \mathcal{H}$ satisfying the normalization condition $\|\Psi\|_{L^2(\mathbb{R}^{3N})} = 1$. The space $\mathcal{H}$, defined as

$$\mathcal{H} = \bigwedge_{i=1}^{N} L^2(\mathbb{R}^3) = \left\{ \Psi \in L^2(\mathbb{R}^{3N}) \;\middle|\; \Psi(x_{p(1)}, \cdots, x_{p(N)}) = \varepsilon(p)\Psi(x_1, \cdots, x_N),\ \forall p \in \mathbb{S}_N \right\}$$

(where $\mathbb{S}_N$ is the group of the permutations of $\{1, \cdots, N\}$ and $\varepsilon(p)$ the parity of p), is the set of antisymmetrized tensor products of N spaces $L^2(\mathbb{R}^3)$. The antisymmetry constraint originates from the fermionic nature of electrons. The spaces $\bigwedge_{i=1}^N H^k(\mathbb{R}^3)$ for $k = 1, 2$ are defined in a similar manner. The electronic density associated with Ψ is the function

$$\rho_\Psi(x) = N \int_{\mathbb{R}^{3(N-1)}} |\Psi(x, x_2, \cdots, x_N)|^2 \, dx_2 \cdots dx_N. \tag{4.1}$$

Clearly,

$$\rho_\Psi \geq 0, \qquad \rho_\Psi \in L^1(\mathbb{R}^3), \qquad \int_{\mathbb{R}^3} \rho_\Psi = N.$$

It can be checked that if $\Psi \in \bigwedge_{i=1}^N H^1(\mathbb{R}^3)$, then $\sqrt{\rho} \in H^1(\mathbb{R}^3)$, which implies in particular that $\rho_\Psi \in L^1(\mathbb{R}^3) \cap L^3(\mathbb{R}^3)$.

The ground state wavefunction Ψ_0 is the normalized solution of lowest energy of the time-independent Schrödinger equation

$$H_N \Psi = E\Psi, \qquad \Psi \in \bigwedge_{i=1}^N H^2(\mathbb{R}^3), \qquad \|\Psi\|_{L^2(\mathbb{R}^{3N})} = 1, \tag{4.2}$$

where H_N is the electronic Hamiltonian. The latter operator is self-adjoint on $\bigwedge_{i=1}^N L^2(\mathbb{R}^3)$, with domain $\bigwedge_{i=1}^N H^2(\mathbb{R}^3)$ and form domain $\bigwedge_{i=1}^N H^1(\mathbb{R}^3)$, and is defined as

$$H_N = -\frac{1}{2} \sum_{i=1}^N \Delta_{x_i} + \sum_{i=1}^N V^{\mathrm{nuc}}(x_i) + \sum_{1 \leqslant i < j \leqslant N} \frac{1}{|x_i - x_j|}. \tag{4.3}$$

The first term in the right-hand side of (4.3) models the kinetic energy of the electrons, the second term the Coulomb interaction between nuclei and electrons and the third term the Coulomb interaction between electrons. For later purposes, we write

$$H_N = T + V_{\mathrm{ne}} + V_{\mathrm{ee}},$$

where

$$T = -\frac{1}{2} \sum_{i=1}^N \Delta_{x_i}, \qquad V_{\mathrm{ne}} = \sum_{i=1}^N V^{\mathrm{nuc}}(x_i), \qquad V_{\mathrm{ee}} = \sum_{1 \leqslant i < j \leqslant N} \frac{1}{|x_i - x_j|}.$$

It is proved in [157] that if the molecular system is neutral ($\sum_{m=1}^M z_m = N$) or positively charged ($\sum_{m=1}^M z_m \geq N$), then the essential spectrum of H_N is an interval of the form $[\Sigma_N, +\infty)$ with $\Sigma_N \leqslant 0$ ($\Sigma_N < 0$ if $N \geq 2$), and its discrete spectrum is an increasing infinite sequence of negative eigenvalues converging to Σ_N. This guarantees the existence of Ψ_0. If E_0, the lowest eigenvalue of H_N is non-degenerate, Ψ_0 is unique up to a global phase, and ρ_{Ψ^0} is therefore uniquely defined by (4.1). If E_0 is degenerate, the ground state electronic density is not unique.

Note that Ψ_0 can also be defined variationally. It is the minimizer of

$$\inf \left\{ \langle \Psi, H_N \Psi \rangle, \;\; \Psi \in \bigwedge_{i=1}^N H^1(\mathbb{R}^3), \; \|\Psi\|_{L^2(\mathbb{R}^{3N})} = 1 \right\}. \tag{4.4}$$

Otherwise stated, it is obtained by minimizing the energy $\langle \Psi, H_N \Psi \rangle$ over the set of all normalized, antisymmetric wavefunctions Ψ of finite energy.

4.1.1.2 The N-body Schrödinger model for non-interacting electrons

Neither the Schrödinger equation (4.2) nor the minimization problem (4.4) can be solved with standard numerical techniques when N exceeds 2 or 3. On the other hand, these problems become rather simple when the interaction between electrons is neglected. In this case, the N-body Hamiltonian is separable and reads

$$H_N^0 = T + V_{\rm ne} = \sum_{i=1}^N h_{x_i}$$

where

$$h_{x_i} = -\frac{1}{2}\Delta_{x_i} + V^{\rm nuc}$$

is a self-adjoint operator on $L^2(\mathbb{R}^3)$ with domain $H^2(\mathbb{R}^3)$ and form domain $H^1(\mathbb{R}^3)$, acting on functions of the variable x_i. It is known that the essential spectrum of h (formerly denoted by h_{x_i}) is $[0,+\infty)$ and that the discrete spectrum of h is an increasing infinite sequence of negative eigenvalues converging to 0. Let us denote by $\varepsilon_1 < \varepsilon_2 \leqslant \varepsilon_3 \leqslant \cdots$ the eigenvalues of h counted with their multiplicities (it can be shown that ε_1 is simple) and let $(\phi_i)_{i\geq 0}$ be an orthonormal family of associated eigenvectors:

$$h\phi_i = \varepsilon_i\phi_i, \qquad \varepsilon_1 < \varepsilon_2 \leqslant \varepsilon_3 \leqslant \cdots, \qquad \phi_i \in H^2(\mathbb{R}^3), \qquad \langle \phi_i, \phi_j \rangle_{L^2(\mathbb{R}^3)} = \delta_{ij}. \tag{4.5}$$

The eigenfunctions ϕ_i are called (molecular) orbitals and the eigenvalues ε_i are called (one-particle) energy levels. It is easy to check that if $\varepsilon_N < \varepsilon_{N+1}$, then

$$\inf\left\{ \langle \Psi, H_N^0 \Psi\rangle, \ \ \Psi \in \bigwedge_{i=1}^N H^1(\mathbb{R}^3), \ \|\Psi\|_{L^2(\mathbb{R}^{3N})} = 1 \right\} \tag{4.6}$$

has a unique solution up to a global phase, given by the determinant (called a Slater determinant)

$$\Psi_0(x_1, \cdots, x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \phi_1(x_1) & \phi_1(x_2) & \cdots & \phi_1(x_N) \\ \phi_2(x_1) & \phi_2(x_2) & \cdots & \phi_2(x_N) \\ \cdot & \cdot & \cdots & \cdot \\ \cdot & \cdot & \cdots & \cdot \\ \cdot & \cdot & \cdots & \cdot \\ \phi_N(x_1) & \phi_N(x_2) & \cdots & \phi_N(x_N) \end{vmatrix}. \tag{4.7}$$

On the other hand, the ground-state of (4.6) is degenerate when $\varepsilon_N = \varepsilon_{N+1}$.

Since $H_N = H_N^0 + V_{\rm ee}$, it is natural to think of the interelectronic potential $V_{\rm ee}$ as a formal perturbation of the reference Hamiltonian H_N^0, and to try to obtain eigenstates of the full N-body Hamiltonian H_N from the eigenstates of H_N^0. This can be completed by adiabatic switching, a procedure described in Section 4.1.2. More precisely, we recall there how eigenstates of H_N^0 can be transformed into eigenstates of H_N using an artificial dynamics, in the case when the initial eigenstate is not degenerate (see [116]). The case of degenerate eigenstates is dealt with in Section 4.1.3.

4.1.2 Adiabatic switching of non-degenerate eigenstates

Adiabatic switching is a crucial ingredient of many-body theory (see Sections 4.1.1.1 and 4.1.1.2). It provides a way to compute eigenstates of a perturbed Hamiltonian $H_0 + V$ from eigenstates of the reference Hamiltonian H_0. The method is presented is an abstract fashion here. A typical application is the case described at the end of the previous section, where $H_0 = H_0^N$ and $V = V_{\rm ee}$.

The basic idea of adiabatic switching is to start from an eigenstate ψ of H_0 (for instance, the ground state), and to very slowly turn on the interaction term V. This is done for instance by following the dynamics generated by the time dependent Hamiltonian $H(t) = H_0 + f(\varepsilon t)V$ on the time interval $[0, \varepsilon^{-1}]$, where f is a smooth function such that $f(0) = 0$ and $f(1) = 1$, and the small parameter $\varepsilon > 0$ eventually vanishes. As we explain below (see Section 4.1.2.2), this procedure is not well defined as such because of a non-convergent phase factor. When the eigenstate belongs to a non-degenerate eigenspace, Gell-Mann and Low solved the problem by dividing out the oscillations by a suitable factor [62] (see (4.12) below). Mathematically, the convergence of this procedure has been proved in 1989 by Nenciu and Rasche [116], elaborating on the adiabatic theorem [19, 61, 94] (see also the more recent contributions [9, 71–73, 113, 115, 119, 140, 144] and references therein).

The situation is more complicated when the eigenstate ψ belongs to a degenerate eigenspace. Understanding for which states adiabatic switching can be performed is precisely the aim of our contributions [H14, H20, H19], described more precisely in Section 4.1.3. We restrict ourselves, for the simplicity of exposition, to the case of non-degenerate eigenvalues in this section.

In practice, since the system of interest is the one described by $H_0 + V$, physicists prefer to consider a switching procedure where the perturbed Hamiltonian is obtained at time 0, with a dynamics started in the distant past from an eigenstate of the reference Hamiltonian ($H(\varepsilon^{-1}t_0) = H_0$ with $t_0 < 0$, and $H(0) = H_0 + V$). Besides, non-compactly supported switching functions may be considered, provided some integrability conditions are satisfied (see Assumption 4.1 below). The prototypical example is

$$H(t) = H_0 + \mathrm{e}^{-\varepsilon|t|}V \tag{4.8}$$

on the time interval $(-\infty, 0]$. This corresponds to a limiting procedure where the switching is performed on a time interval $[\varepsilon^{-1}t_0, 0]$, and the limit $t_0 \to -\infty$ is then considered (see the discussion at the end of Section 4.1.2.1). The choice (4.8) is motivated by the greater simplicity of some algebraic computations in the evaluation of the Green's functions [59]. Since this is the physically relevant case, we therefore restrict ourselves in the sequel to Hamiltonians of the form (4.8), see (4.10) below.

4.1.2.1 Switching procedure

Consider a Hilbert space $\mathcal{H}$, a self-adjoint operator H_0, with dense domain $D(H_0) \subset \mathcal{H}$, and a symmetric perturbation V (such as the multiplication by a real-valued potential), H_0-bounded with relative bound $a < 1$. For instance, the interelectronic repulsion operator V_{ee} is relatively bounded with respect to the N-body Hamiltonian H_0^N of non-interacting electrons, with relative bound 0 (see Section 4.1.1.2 for a definition of these operators).

Then, according to the Kato-Rellich theorem (Theorem X.12 in [124]), $H_0 + \lambda V$ is self-adjoint on $D(H_0)$ for any $0 \leqslant \lambda \leqslant 1$. We denote

$$\widetilde{H}(\lambda) = H_0 + \lambda V, \tag{4.9}$$

with $\lambda \in [0, 1]$, and introduce, for $\tau \in (-\infty, 0]$,

$$H(\tau) = \widetilde{H}(f(\tau)) = H_0 + f(\tau)\, V, \tag{4.10}$$

where the switching function f has values in $[0, 1]$ (in order for the operator $H(\tau)$ to be well-defined as a self-adjoint operator on $D(H_0)$). For the subsequent analysis, we assume that

Assumption 4.1. *The switching function $f : (-\infty, 0] \to [0, 1]$ is a C^2 function such that*

(i) $f(0) = 1$ and $\lim_{\tau \to -\infty} f(\tau) = 0$;
(ii) $f, f', f'' \in L^1((-\infty, 0])$.

The most common choice in practice is $f(\tau) = \mathrm{e}^{\tau}$. The assumption $f \in C^2$ ensures that the adiabatic evolution, which is a unitary evolution introduced for technical reasons in the proof, is well-defined (see [144]).

We denote by $U_\varepsilon(s, s_0)$ the unitary evolution generated by $H(\varepsilon s)$, *i.e.* the unique solution (which is well-defined by Theorem X.70 in [124]) of the problem:

$$\mathrm{i}\frac{dU_\varepsilon(s,s_0)}{ds} = H(\varepsilon s)\, U_\varepsilon(s,s_0), \qquad U_\varepsilon(s_0,s_0) = 1.$$

It is actually more convenient to rescale the time and to consider a macroscopic time $t = \varepsilon s$. The unitary evolution $U^\varepsilon(t, t_0)$ in terms of the macroscopic time is the solution of

$$\mathrm{i}\varepsilon\frac{dU^\varepsilon(t,t_0)}{dt} = H(t)U^\varepsilon(t,t_0), \qquad U^\varepsilon(t_0,t_0) = 1.$$

In order to remove trivial divergent phase factors, evolution operators should be considered in the interaction picture:

$$U^\varepsilon_{\mathrm{int}}(t,t_0) = \mathrm{e}^{\mathrm{i}tH_0/\varepsilon}\, U^\varepsilon(t,t_0)\, \mathrm{e}^{-\mathrm{i}t_0H_0/\varepsilon}.$$

To see why this is necessary, consider the case when $V = 0$. Then, an eigenstate ψ of H_0, with eigenvalue E, evolves as

$$U^\varepsilon(t,t_0)\psi = \exp\left(-\mathrm{i}\frac{t-t_0}{\varepsilon}\right)\psi,$$

while $U^\varepsilon_{\mathrm{int}}(t,t_0)\psi = \psi$. The interaction picture allows to get rid of the divergence of the phase (at fixed ε) related to the free evolution generated by H_0, and therefore allows to consider the limit where $t_0 \to -\infty$. Indeed, when $V \neq 0$, it is easy to show that $U^\varepsilon_{\mathrm{int}}(t,-\infty)\psi = \lim_{t_0\to-\infty} U^\varepsilon_{\mathrm{int}}(t,t_0)\psi$ exists for $\psi \in D(H_0)$ (for instance, by rewriting this operator as the integral of its derivative with respect to t_0).

4.1.2.2 The Gell-Mann and Low wavefunction

Once the phase factors related to the free evolution $\mathrm{e}^{-\mathrm{i}tH_0}$ have been removed, the state $U^\varepsilon_{\mathrm{int}}(0,-\infty)\psi$ is well defined for any $\varepsilon > 0$. The key point is that this state does not have a limit as $\varepsilon \to 0$ since it carries in general a phase factor of the form $\mathrm{e}^{-\mathrm{i}\theta/\varepsilon}$. To make this statement precise, we consider in the remainder of this section the case of a non-degenerate eigenvalue $\widetilde{E}(\lambda)$ of $\widetilde{H}(\lambda)$ (defined in (4.9)), isolated from the remainder of the spectrum. Note that $\widetilde{E}$ can be chosen to be a smooth function since, by the results of [95], the projectors and eigenvalues of $\widetilde{H}(\lambda)$ can be chosen to be real analytic functions of λ on an open interval containing $[0,1]$.

Assumption 4.2 (Gap condition). *There is a gap between the eigenvalue $\widetilde{E}$ and the remainder of the spectrum, in the sense that*

$$\Delta(\lambda) = \mathrm{dist}\left\{\widetilde{E}(\lambda), \sigma\left(\widetilde{H}(\lambda)\right)\setminus\{\widetilde{E}(\lambda)\}\right\}$$

is bounded from below by a positive constant:

$$\inf_{\lambda\in[0,1]} \Delta(\lambda) = \Delta^* > 0.$$

In accordance with (4.10), we introduce $E(\tau) = \widetilde{E}(f(\tau))$. When Assumptions 4.1 and 4.2 hold, it can be proved that an eigenstate ψ associated with the eigenvalue $\widetilde{E}(0) = E(-\infty)$ of the reference Hamiltonian H_0 evolves under the switching procedure as [116]

$$U^\varepsilon_{\mathrm{int}}(0,-\infty)\psi = \mathrm{e}^{-\mathrm{i}\theta/\varepsilon}\Omega\psi + R_\varepsilon, \qquad \theta = \int_{-\infty}^{0}\Big(E(t) - E(-\infty)\Big)dt, \tag{4.11}$$

where $\Omega\psi$ is an eigenstate of $H_0 + V$ and $\|R_\varepsilon\| \leqslant C\varepsilon$. Note that θ is well defined since

$$\int_{-\infty}^{0} |E(t) - E(-\infty)|\, dt \leqslant \alpha \int_{-\infty}^{0} |f| < +\infty,$$

where the constant α is such that $|\widetilde{E}(\lambda) - \widetilde{E}(0)| \leqslant \alpha|\lambda|$ (this constant exists since the eigenvalue $\widetilde{E}$ is a smooth function of λ).

The expression (4.11) allows to fully understand the origin of the divergence in the switching procedure. It is then easy to remove the divergence by introducing a suitable ratio. This is the Gell-Mann wavefunction:

$$\Psi = \lim_{\varepsilon \to 0} \frac{U^\varepsilon_{\rm int}(0, -\infty)\psi}{\langle\, \psi, U^\varepsilon_{\rm int}(0, -\infty)\psi \,\rangle} = \frac{\Omega\psi}{\langle \psi, \Omega\psi \rangle}. \tag{4.12}$$

In order for this ratio to be well defined, the denominator has to be different from 0. It can be shown that this is the case when $\|P(-\infty) - P(0)\| < 1$, where $P(t)$ is the orthogonal projector onto the eigensubspace associated with the eigenvalue $E(t)$.

4.1.3 Adiabatic switching of degenerate eigenstates

The physics community realized about fifty years ago [17] that a generalization of the Gell-Mann and Low formula is needed when starting from a state associated to a degenerate eigenvalue of H_0. Degenerate states, and in particular degenerate ground states, arise in many practical situations, for instance when the system is an atom or a molecule containing unfilled shells (this corresponds to the condition $\varepsilon_{N+1} = \varepsilon_N$ in (4.5)). This problem has been discussed in several fields, including nuclear physics, solid state physics, quantum chemistry and atomic physics, see the references in [H14, H19].

More precisely, the aim is to find the initial states ψ in (4.12) for which the switching can be performed. Indeed, the Gell-Mann and Low formula (4.12) is not applicable in general when the initial state is chosen at random in the degenerate subspace, as illustrated in the simple model analytically studied in [H14], where

$$H_0 = \begin{pmatrix} \mu - \delta & 0 \\ 0 & \mu + \delta \end{pmatrix}, \qquad V = \begin{pmatrix} 0 & v \\ v & 0 \end{pmatrix}, \tag{4.13}$$

for some $v \neq 0$. The switching procedure is well defined when $\delta \neq 0$. On the other hand, in the case of a degenerate eigenvalue ($\delta = 0$), the switching procedure cannot be performed for almost all initial conditions in the degenerate eigenspace. There are only two directions for which the procedure makes sense. They correspond to limiting eigenstates of the operators $H_0 + \lambda V$ as $\lambda > 0$ goes to 0. In this very simple setting, they turn out to be eigenstates of V.

A more precise mathematical analysis shows that the eigenstates for which the switching procedure is well defined are eigenstates of the restriction of the perturbation operator to the degenerate eigenspace, that is, eigenstates of $\mathcal{P}_0 V \mathcal{P}_0\big|_{\mathcal{E}_0}$ (where $\mathcal{P}_0$ is the orthogonal projection onto $\mathcal{E}_0$, the degenerate eigenspace; see (4.14) below for a precise definition). The result, as in the non degenerate case, is based on the mathematical analysis of adiabatic problems.

4.1.3.1 Spectral structure of the problem

As usual in results from adiabatic theory, we need some assumptions on the spectrum of the operators under considerations, in particular some gap conditions. A schematic representation of the spectrum we have in mind is provided in Figure 4.1.

Throughout this section, we assume that the spectrum has the following structure.

Assumption 4.3 (Structure of the spectrum). *The spectrum of $\widetilde{H}(\lambda) = H_0 + \lambda V$ (for $\lambda \in [0,1]$) consists of two disconnected components*

$$\sigma\left(\widetilde{H}(\lambda)\right) = \sigma_N(\lambda) \cup \left(\sigma\left(\widetilde{H}(\lambda)\right) \setminus \sigma_N(\lambda)\right)$$

where $\sigma_N(\lambda)$ is a finite subset of the discrete spectrum:

$$\sigma_N(\lambda) = \left\{\widetilde{E}_j(\lambda),\ j = 1, \dots, N\right\} \subset \sigma_{\mathrm{disc}}\left(\widetilde{H}(\lambda)\right),$$

corresponding to an initially degenerate eigensubspace: there exists an integer $N > 1$ and $E_0 \in \mathbb{R}$ such that $\widetilde{E}_j(0) = E_0$ for all $1 \leqslant j \leqslant N$.

Assumption 4.4 (Gap condition). *There is a gap between the two parts of the spectrum, in the sense that:*

$$\Delta(\lambda) = \min_{j=1,\dots,N}\left[\inf\left(\left|\widetilde{E}_j(\lambda) - E\right|,\ E \in \sigma\left(\widetilde{H}(\lambda)\right) \setminus \left\{\widetilde{E}_1(\lambda), \dots, \widetilde{E}_N(\lambda)\right\}\right)\right],$$

is bounded from below by a positive constant:

$$\inf_{\lambda\in[0,1]} \Delta(\lambda) = \Delta^* > 0.$$

The projectors associated with the N eigenvalues $\widetilde{E}_j(\lambda)$ are denoted by $\widetilde{P}_m(\lambda)$, for $1 \leqslant m \leqslant M$ with $M \leqslant N$. The case $M < N$ corresponds to the case when an eigenvalue $\widetilde{E}_m(\lambda)$ is permanently degenerate on the interval $[0,1]$. The projector onto the subspace orthogonal to the eigenspace spanned by the N eigenvectors is $\widetilde{P}_{N+1}(\lambda) = 1 - \sum_{m=1}^{M} \widetilde{P}_m(\lambda)$. We denote in the sequel

$$\mathcal{P}_0 = \sum_{m=1}^{M} \widetilde{P}_m(0) \tag{4.14}$$

the projector onto the eigenspace $\mathcal{E}_0 = \mathrm{Ran}(\mathcal{P}_0)$ spanned by the N degenerate eigenstates of H_0. Recall that, by the results of [95], the projectors and eigenvalues of $\widetilde{H}(\lambda)$ can be chosen to be real analytic functions of λ on an open interval containing $[0,1]$.

For simplicity, we assume that the perturbation V is sufficient to split the degeneracy (so that $M = N$), in the sense that the following assumption holds true.

Assumption 4.5 (Degeneracy splitting). *The finite rank self-adjoint operator $\mathcal{P}_0 V \mathcal{P}_0 : \mathcal{E}_0 \to \mathcal{E}_0$ has non-degenerate eigenvalues, and there is a gap between the N eigenvalues $\widetilde{E}_k$ ($1 \leqslant k \leqslant N$) in the interval $(0,1]$: for any $\lambda^* > 0$, there exists α (depending on λ^*) such that*

$$\min_{\lambda^* \leqslant \lambda \leqslant 1} \min_{k \neq l} \left|\widetilde{E}_k(\lambda) - \widetilde{E}_l(\lambda)\right| \geqslant \alpha > 0. \tag{4.15}$$

This implies that the projectors $\widetilde{P}_j(\lambda)$ are rank-1 projectors for any $\lambda > 0$ (since the perturbation V is sufficient to split the eigensubspaces, and the gap condition on $(0,1]$ ensures that no eigenvalue crossing can happen). In fact, Assumption 4.5 may be relaxed in several ways, see the discussion in [H20].

4.1.3.2 Well-posedness of the switching

The switching procedure is the same as the one described in Section 4.1.2.1, except that, for technical reasons, we require in addition to Assumption 4.1 that f is non-decreasing.

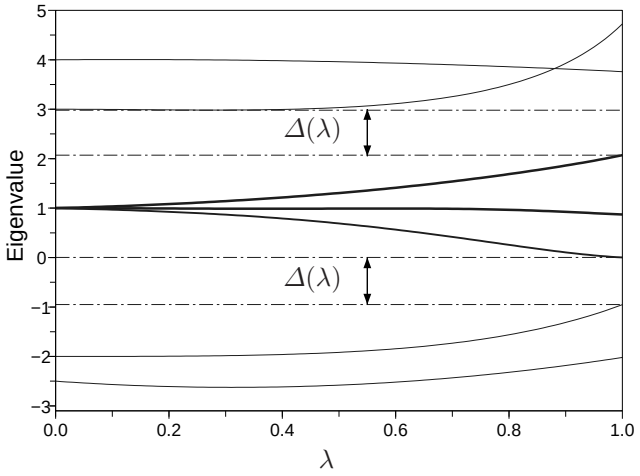


Fig. 4.1. Splitting of the eigenspace $\mathcal{E}_0$ of the initial Hamiltonian H_0 by the applied perturbation. The three eigenvalues of interest, which all start from $E = 1$ at $\lambda = 0$, are plotted with a fat solid line. The remaining parts of the spectrum (eigenvalues in thin solid line in this case) are isolated from the portion of the spectrum of interest.

We denote by $P_j(\tau)$ the eigenprojectors and eigenvalues corresponding to the N eigenvalues $E_j(\tau)$ of $H(\tau)$; also, $P_{N+1}(\tau) = 1 - \sum_{k=1}^{N} P_k(\tau)$. Of course, $P_j(\tau) = \widetilde{P}_j(f(\tau))$ and $E_j(\tau) = \widetilde{E}_j(f(\tau))$. We are now in position to state the main result of [H20].

Theorem 4.1. *Suppose that the gap conditions on H_0 and V (Assumptions 4.3 and 4.4) are satisfied, and that the perturbation term V lifts the degeneracy (Assumption 4.5). Consider a non-decreasing switching function f satisfying Assumption 4.1. Let $(\psi_1, \dots, \psi_N)$ be an orthonormal basis of $\mathcal{E}_0$ which diagonalizes the bounded operator $\mathcal{P}_0 V \mathcal{P}_0\big|_{\mathcal{E}_0}$. Then, the limit*

$$\Psi_j = \lim_{\varepsilon \to 0} \frac{U^{\varepsilon}_{\rm int}(0, -\infty)\psi_j}{\langle\, \psi_j, U^{\varepsilon}_{\rm int}(0, -\infty)\psi_j \,\rangle} \tag{4.16}$$

exists and is an eigenstate of $H_0 + V$ associated with the eigenvalue $E_j(0)$, provided

$$\|P_j(-\infty) - P_j(0)\| < 1. \tag{4.17}$$

The labelling of the basis $(\psi_1, \dots, \psi_N)$ is a priori unknown, but a relabelling can be performed a posteriori, after the switching, depending on which eigenstate of $H_0 + V$ is obtained.

As an intermediate step in the proof, the eigenprojector $P_j(0)$ and a corresponding eigenfunction Ψ_j can be recovered by Kato's geometric evolution [94].

Definition 4.1. *The Kato evolution operator $A(s, s_0)$, for $s, s_0 \in \mathbb{R}$ is the unique solution of the problem*

$$\frac{dA(s, s_0)}{ds} = K(s)\, A(s, s_0), \quad A(s_0, s_0) = 1, \tag{4.18}$$

with

$$K(s) = -\sum_{j=1}^{N+1} P_j(s)\, \frac{dP_j}{ds}(s).$$

By our assumptions, the operator $K(s)$ is uniformly bounded. The Kato evolution operator is a unitary operator which intertwines the spectral subspaces of $H(s)$ and $H(s_0)$, in the sense that

$$A(s, s_0)P_j(s_0) = P_j(s)A(s, s_0).$$

Our assumptions ensure that the limit $A(s, -\infty) = \lim_{s_0 \to -\infty} A(s, s_0)$ is well-defined.

We can then prove the following result, where no condition analogous to (4.17) is assumed.

Proposition 4.1. *Let Assumptions 4.1, 4.3, 4.4 and 4.5 be satisfied. Let $(\psi_1, \dots, \psi_N)$ be an orthonormal basis of $\mathcal{E}_0$ which diagonalizes the operator $\mathcal{P}_0 V \mathcal{P}_0\big|_{\mathcal{E}_0}$. Then*

$$\Psi_j = A(0, -\infty)\psi_j$$

is an eigenvector of $H_0 + V$.

It is actually much simpler to consider the geometric evolution operator A rather than the evolution operator $U^\varepsilon_{\rm int}$ since less conditions on H_0 and V are required. Indeed, there is no ratio to consider in order to remove a divergent phase. However, the many-body theory used in physics is defined in terms of $U^\varepsilon_{\rm int}$ and not in terms of A (see Section 4.1.4).

4.1.3.3 Sketch of the proof

We shortly sketch the structure of the proof of Theorem 4.1, which is completed in four steps:

(i) first, we use the Kato geometric evolution backward in time, in order to identify, though in a non explicit manner, the initial subspaces of $\mathcal{P}_0$ whose vectors can be considered as convenient initial states;
(ii) in a second step, we give an explicit description of these initial subspaces, in terms of the eigenvectors of $\mathcal{P}_0 V \mathcal{P}_0\big|_{\mathcal{E}_0}$. At this stage, we are already in position to prove Proposition 4.1;
(iii) then, we show how the limit of the full evolution $U^\varepsilon_{\rm int}$ can be related to the geometric evolution as $\varepsilon \to 0$. A first step is to introduce an intermediate concept, the adiabatic evolution, which takes some dynamics into account (arising from the Hamiltonian operator). The adiabatic evolution is also an intertwiner. Since intertwiners differ only by a phase (in a sense to be made precise), and, provided this phase can be removed, the adiabatic evolution can be reduced to the geometric evolution $A(0, -\infty)$;
(iv) the last point is to show that the limit as $\varepsilon \to 0$ of the full evolution agrees with the limit of the adiabatic evolution.

Steps (iii) and (iv) are straightforward extensions of previous results in adiabatic theory, and our proofs are based on the paper by Nenciu and Rasche [116] for (iii) and the book by Teufel [144] for (iv). The main point of our proof is the identification of the initial subspaces in (ii) using results of perturbation theory.

4.1.4 Physical application: definition of the Green's functions

The previous results can be used to rigorously define correlation functions of two operators A, B (see the definition (4.19) below). The extension to Green's functions, where the operators A, B are replaced by field operators, is discussed in [H19]. Statistical and nonequilibrium Green's functions are also considered there.

We consider for simplicity bounded operators A, B, although the argument can be extended to more general cases. The operators A and B read, in the Heisenberg picture:

$$A_{\rm hsnbrg}(t) = \mathrm{e}^{\mathrm{i}tH} A\, \mathrm{e}^{-\mathrm{i}tH}, \qquad B_{\rm hsnbrg}(t) = \mathrm{e}^{\mathrm{i}tH} B\, \mathrm{e}^{-\mathrm{i}tH},$$

and, in the interaction picture:

$$A_{\rm int}(t) = \mathrm{e}^{\mathrm{i}tH_0} A\, \mathrm{e}^{-\mathrm{i}tH_0}, \qquad B_{\rm int}(t) = \mathrm{e}^{\mathrm{i}tH_0} B\, \mathrm{e}^{-\mathrm{i}tH_0}.$$

The correlation function is defined as

$$C_{A,B}(t,t') = \langle \psi, T\left[A_{\rm hsnbrg}(t) B_{\rm hsnbrg}(t')\right] \psi \rangle\,, \tag{4.19}$$

where ψ an eigenvector of $H_0 + V$ satisfying $\|\psi\| = 1$, and T is the time-ordering operator:

$$T\left[A_{\rm hsnbrg}(t) B_{\rm hsnbrg}(t')\right] = \begin{cases} A_{\rm hsnbrg}(t) B_{\rm hsnbrg}(t') \text{ if } t > t', \\ B_{\rm hsnbrg}(t') A_{\rm hsnbrg}(t) \text{ if } t < t'. \end{cases}$$

The aim is to rewrite $C_{A,B}$ in terms of an expectation value with respect to ψ_0, an eigenvector of H_0 (belonging to a possibly degenerate eigensubspace). To this end, we consider an initial state ψ_0 for which the Gell-Mann and Low switching can be performed (see Theorem 4.1), and for which ψ is recovered. Note first that $U_{\varepsilon,\rm int}(0,-\infty) = U^{\varepsilon}_{\rm int}(0,-\infty)$ for any $\varepsilon > 0$, so that (4.16) can be rewritten as

$$\psi = \lim_{\varepsilon \to 0} \frac{U_{\varepsilon,\rm int}(0,-\infty)\psi_0}{\langle\, \psi_0, U_{\varepsilon,\rm int}(0,-\infty)\psi_0 \,\rangle}.$$

Similarly,

$$\psi = \lim_{\varepsilon \to 0} \frac{U_{\varepsilon,\rm int}(0,+\infty)\psi_0}{\langle\, \psi_0, U_{\varepsilon,\rm int}(0,+\infty)\psi_0 \,\rangle} \tag{4.20}$$

when the switching is done using $H_0 + f(-\varepsilon t)V$ and $t \geqslant 0$. We are then in position to obtain an expression of the correlation function in terms of an eigenstate of H_0. Consider first the case $t > t'$:

$$\begin{aligned} T\left[A_{\rm hsnbrg}(t) B_{\rm hsnbrg}(t')\right] \psi &= A_{\rm hsnbrg}(t) B_{\rm hsnbrg}(t') \psi \\ &= \lim_{\varepsilon \to 0} U_{\varepsilon,\rm int}(t,0)^* A_{\rm int}(t)\, U_{\varepsilon,\rm int}(t,t')\, B_{\rm int}(t')\, U_{\varepsilon,\rm int}(t',0)\psi, \end{aligned}$$

where the second equality is a consequence of the strong convergence $U_{\varepsilon,\rm int}(t,0) \to \mathrm{e}^{\mathrm{i}tH_0}\mathrm{e}^{-\mathrm{i}tH}$ as $\varepsilon \to 0$ (for a given $t \in \mathbb{R}$). Therefore,

$$\begin{aligned} C_{A,B}(t,t') &= \lim_{\varepsilon \to 0} \langle \psi, U_{\varepsilon,\rm int}(t,0)^* A_{\rm int}(t)\, U_{\varepsilon,\rm int}(t,t')\, B_{\rm int}(t')\, U_{\varepsilon,\rm int}(t',0)\psi \rangle \\ &= \lim_{\varepsilon \to 0} \frac{\langle \psi, U_{\varepsilon,\rm int}(t,0)^* A_{\rm int}(t)\, U_{\varepsilon,\rm int}(t,t')\, B_{\rm int}(t')\, U_{\varepsilon,\rm int}(t',0)\psi \rangle}{\langle \psi, \psi \rangle} \\ &= \lim_{\varepsilon \to 0} \frac{\langle \psi_0, U_{\varepsilon,\rm int}(0,+\infty)^* U_{\varepsilon,\rm int}(t,0)^* A_{\rm int}(t)\, U_{\varepsilon,\rm int}(t,t')\, B_{\rm int}(t')\, U_{\varepsilon,\rm int}(t',0)\, U_{\varepsilon,\rm int}(0,-\infty)\psi_0 \rangle}{\langle \psi_0,\, U_{\varepsilon,\rm int}(+\infty,0)\, U_{\varepsilon,\rm int}(0,-\infty)\psi_0 \rangle} \\ &= \lim_{\varepsilon \to 0} \frac{\langle \psi_0, U_{\varepsilon,\rm int}(+\infty,t) A_{\rm int}(t)\, U_{\varepsilon,\rm int}(t,t')\, B_{\rm int}(t')\, U_{\varepsilon,\rm int}(t',-\infty)\psi_0 \rangle}{\langle \psi_0,\, U_{\varepsilon,\rm int}(+\infty,-\infty)\psi_0 \rangle} \\ &= \lim_{\varepsilon \to 0} \frac{\langle \psi_0,\, T\left[A_{\rm int}(t)\, B_{\rm int}(t')\, U_{\varepsilon,\rm int}(+\infty,-\infty)\right] \psi_0 \rangle}{\langle \psi_0,\, U_{\varepsilon,\rm int}(+\infty,-\infty)\psi_0 \rangle}. \end{aligned}$$

In the last equality, the notation

$$T[A_{\rm int}(t)\, B_{\rm int}(t')\, U_{\varepsilon,\rm int}(+\infty,-\infty)] = U_{\varepsilon,\rm int}(+\infty,t) A_{\rm int}(t)\, U_{\varepsilon,\rm int}(t,t')\, B_{\rm int}(t')\, U_{\varepsilon,\rm int}(t',-\infty)$$

is motivated by the fact that $U_{\varepsilon,\rm int}(+\infty,t) U_{\varepsilon,\rm int}(t,t') U_{\varepsilon,\rm int}(t',-\infty) = U_{\varepsilon,\rm int}(+\infty,-\infty)$, so that the right-hand side of the latter identity can be seen as the time ordering of the product of five

operators appearing on the left. The same result holds for $t < t'$. The final expression for $C_{A,B}$ is the basis for a perturbative treatment of the Green's function, where the operators $U_{\varepsilon,\mathrm{int}}(+\infty,-\infty)$ in the numerator and denominator are expanded using Feynman diagrams (see [59, Chapter 3]).

4.2 Evolution of defects in crystals

This section describes our work [H30], whose aim was to extend the results on the static polarization of crystals [24] to the time-dependent setting. Crystals are electronic systems composed of an infinite number of nuclei and electrons, the nuclei being periodically arranged on a lattice. The analysis presented in [H30] allows to place on rigorous grounds well-known results from the physics literature on the frequency-dependent dielectric permittivity of crystals.

We start by recalling in Section 4.2.1 the mathematical framework to describe crystals and their local defects. We then turn in Sections 4.2.2 and 4.2.3 to the response of the crystal to an external perturbing field. Physically, it is expected that the material responds by a global charge redistribution. When the external perturbation is weak, or, more precisely, when only the linear response is considered, the perturbation of the electronic density can be expressed as the time convolution of some causal response function (the dielectric permittivity) with the applied external electric field. The case of a crystal subjected to an *effective* external field is considered in Section 4.2.2. Now, in practice, the effective external potential should be replaced by an external perturbation plus the electronic response of the crystal to this external perturbation. Since crystals are described by nonlinear models, the electronic response turns out to be the solution of a self-consistent evolution equation. This is made precise in Section 4.2.3, where we also provide an expression of the macroscopic dielectric permittivity in terms of the band structure of the crystal (by some homogenization limit).

4.2.1 A quantum description of crystals

We described in Section 4.1.1 the electronic states of a set of N non-interacting electrons in terms of their orbitals. Such a description cannot easily be extended to infinite systems such as crystals, where the number of orbitals is infinite. For this reason, we introduce in Section 4.2.1.1 a formulation based on the concept of one-particle density operators, abbreviated as density operators, and relate the description of electronic states in terms of wavefunctions and density operators in Section 4.2.1.2. We then present in Section 4.2.1.3 the Hartree model for systems composed of a finite number of particles, which is one important nonlinear model approximating the Schrödinger equation. The Hartree model for crystals is obtained by passing to the thermodynamic limit on the model for finite systems (see Section 4.2.1.4). Finally, we recall in Section 4.2.1.5 the framework proposed in [23] to describe defects in perfect crystals.

4.2.1.1 Density operators

The (one-particle) density operator of a system of N electrons is an element of the convex set

$$\mathcal{D}_N = \Big\{ \gamma \in \mathcal{S}(L^2(\mathbb{R}^3)) \;\Big|\; 0 \leqslant \gamma \leqslant 1,\ \mathrm{Tr}(\gamma) = N \Big\},$$

where $\mathcal{S}(L^2(\mathbb{R}^3)) \subset \mathcal{B}(L^2(\mathbb{R}^3))$ is the subset of bounded, self-adjoint operators on $L^2(\mathbb{R}^3)$. Recall that the notation $A \leqslant B$ for $A, B \in \mathcal{S}(L^2(\mathbb{R}^3))$ means that $\langle \psi, A\psi \rangle \leqslant \langle \psi, B\psi \rangle$ for all $\psi \in L^2(\mathbb{R}^3)$.

A density operator $\gamma \in \mathcal{D}_N$ is trace-class. Recall that a bounded linear operator A on $L^2(\mathbb{R}^3)$ is said to be trace-class [125, 139] if $\sum_i \left\langle \phi_i, \sqrt{A^*A}\phi_i \right\rangle_{L^2} < \infty$ for some (hence, all) orthonormal basis (ϕ_i) of $L^2(\mathbb{R}^3)$. Then $\mathrm{Tr}(A) = \sum_i \langle \phi_i, A\phi_i \rangle_{L^2}$ is well-defined and does not depend on the chosen basis. A density operator $\gamma \in \mathcal{D}_N$ can be diagonalized in an orthonormal basis:

$$\gamma = \sum_{i=1}^{+\infty} n_i |\phi_i\rangle\langle\phi_i|, \tag{4.21}$$

with $\langle \phi_i, \phi_j \rangle_{L^2(\mathbb{R}^3)} = \delta_{ij}$, and where operators such as $P = |f\rangle\,\langle g|$ (for $f, g \in L^2(\mathbb{R}^3)$) are bounded operators defined for $\phi \in L^2(\mathbb{R}^3)$ by $P\phi = \langle g, \phi \rangle f$. The eigenvalues n_i in (4.21) are called occupation numbers; the eigenfunctions ϕ_i are called natural orbitals. The conditions $0 \leqslant \gamma \leqslant 1$ and $\mathrm{Tr}(\gamma) = N$ are respectively equivalent to

$$0 \leqslant n_i \leqslant 1, \qquad \sum_{i=1}^{+\infty} n_i = N.$$

The fact that $0 \leqslant n_i \leqslant 1$ is a mathematical translation of the Pauli exclusion principle, stipulating that each quantum state $|\phi_i\rangle$ is occupied by at most one electron. The sum of the occupation numbers is equal to N, the number of electrons in the system. The density associated with γ is defined by

$$\rho_\gamma(x) = \sum_{i=1}^{+\infty} n_i |\phi_i(x)|^2, \tag{4.22}$$

this definition being independent of the choice of the orthonormal basis $(\phi_i)_{i\geq 1}$ in (4.21), and satisfies

$$\rho_\gamma \geq 0, \qquad \rho_\gamma \in L^1(\mathbb{R}^3), \qquad \int_{\mathbb{R}^3} \rho_\gamma = N.$$

The kinetic energy of the density operator γ is defined as

$$T(\gamma) = \frac{1}{2}\mathrm{Tr}(|\nabla|\gamma|\nabla|),$$

and can be finite or infinite. Recall that the operator $|\nabla|$ is the unbounded self-adjoint operator on $L^2(\mathbb{R}^3)$ with domain $H^1(\mathbb{R}^3)$ defined by

$$\forall \phi \in H^1(\mathbb{R}^3), \qquad \mathcal{F}(|\nabla|\phi)(k) = |k|\mathcal{F}(\phi)(k),$$

where $\mathcal{F}$ is the unitary Fourier transform

$$\mathcal{F}\phi(k) = \widehat{\phi}(k) = \frac{1}{(2\pi)^{3/2}} \int_{\mathbb{R}^3} \phi(x)\, \mathrm{e}^{-\mathrm{i}k\cdot x}\, dx. \tag{4.23}$$

The kinetic energy of a density operator γ decomposed as (4.21) is finite if and only if each ϕ_i is in $H^1(\mathbb{R}^3)$ and $\sum_{i=1}^{+\infty} n_i \|\nabla\phi_i\|^2_{L^2(\mathbb{R}^3)} < \infty$, in which case

$$T(\gamma) = \frac{1}{2}\sum_{i=1}^{+\infty} n_i \|\nabla\phi_i\|^2_{L^2(\mathbb{R}^3)}.$$

As $|\nabla|$ is the square root of $-\Delta$ (*i.e.* $|\nabla|$ is self-adjoint, positive and $|\nabla|^2 = -\Delta$), the element $\mathrm{Tr}(|\nabla|\gamma|\nabla|)$ of $\mathbb{R}_+ \cup \{+\infty\}$ is often denoted by $\mathrm{Tr}(-\Delta\gamma)$. Using this notation, we can define the convex set $\mathcal{P}_N$ of the density operators of finite energy as

$$\mathcal{P}_N = \Big\{ \gamma \in \mathcal{S}(L^2(\mathbb{R}^3)) \;\Big|\; 0 \leqslant \gamma \leqslant 1,\ \mathrm{Tr}(\gamma) = N,\ \mathrm{Tr}(-\Delta\gamma) < \infty \Big\}.$$

Finally, it is useful to introduce the integral kernel of a density operator $\gamma \in \mathcal{P}_N$, which is called a (one-particle) density matrix, and is usually also denoted by γ. It is by definition the function $\gamma \in L^2(\mathbb{R}^3 \times \mathbb{R}^3)$ such that

$$\forall \phi \in L^2(\mathbb{R}^3), \quad (\gamma\phi)(x) = \int_{\mathbb{R}^3} \gamma(x,x')\phi(x')\,dx'. \tag{4.24}$$

The expression of the density matrix γ in terms of natural orbitals and occupation numbers thus reads

$$\gamma(x,x') = \sum_{i=1}^{+\infty} n_i \overline{\phi_i(x)}\,\phi_i(x').$$

Formally $\rho_\gamma(x) = \gamma(x,x)$ and this relation makes sense as soon as the density matrix γ has a trace on the three-dimensional vector subspace $\big\{(x,x),\, x \in \mathbb{R}^3\big\}$ of $\mathbb{R}^3 \times \mathbb{R}^3$.

4.2.1.2 Electronic states

Let us now clarify the link between the description of electronic structures in terms of wavefunctions and the one in terms of density operators. The density matrix associated with a wavefunction $\Psi \in \wedge_{i=1}^N L^2(\mathbb{R}^3)$ such that $\|\Psi\|_{L^2(\mathbb{R}^{3N})} = 1$ is the function of $L^2(\mathbb{R}^3 \times \mathbb{R}^3)$ defined as

$$\gamma_\Psi(x,x') = N \int_{\mathbb{R}^{3(N-1)}} \overline{\Psi(x,x_2,\cdots,x_N)}\Psi(x',x_2,\cdots,x_N)\,dx_2\cdots dx_N, \tag{4.25}$$

and the corresponding density operator is

$$\forall \phi \in L^2(\mathbb{R}^3), \quad (\gamma_\Psi\phi)(x) = \int_{\mathbb{R}^3} \gamma_\Psi(x,x')\phi(x')\,dx'. \tag{4.26}$$

It is easy to see that the density operator γ_Ψ is in $\mathcal{D}_N$. Under the additional assumption that Ψ belongs to $\wedge_{i=1}^N H^1(\mathbb{R}^3)$, the density operator has better regularity properties and belongs to $\mathcal{P}_N$. In addition, the definition (4.1) of the density associated with Ψ agrees with the definition (4.22) of the density associated with γ_Ψ, *i.e.* $\rho_\Psi = \rho_{\gamma_\Psi}$, and the definitions of the kinetic energy coincide when $\Psi \in \wedge_{i=1}^N H^1(\mathbb{R}^3)$, namely $\langle \Psi, T\Psi\rangle = T(\gamma_\Psi)$. Note however that not all elements of $\mathcal{D}_N$ and $\mathcal{P}_N$ can be written as (4.25). In general, the elements of these sets are convex combinations of pure states (4.25), and are called mixed states.

We can now reformulate the electronic structure problem for a system of N *non-interacting* electrons (see Section 4.1.1.2), in terms of density operators:

(1) The energy of a wavefunction $\Psi \in \wedge_{i=1}^N H^1(\mathbb{R}^3)$ is a linear form with respect to the density operator γ_Ψ:

$$\langle \Psi, H_N^0 \Psi\rangle = E^0_{\rho^{\rm nuc}}(\gamma_\Psi), \qquad E^0_{\rho^{\rm nuc}}(\gamma) = \mathrm{Tr}\left(-\frac{1}{2}\Delta\gamma\right) + \int_{\mathbb{R}^3} \rho_\gamma V^{\rm nuc};$$

(2) The ground state density matrix, that is, the density operator associated with the ground state wavefunction Ψ^0 defined by (4.6), is the orthogonal projector (for the L^2 inner product) on the space $\mathrm{Span}(\phi_1,\cdots,\phi_N)$:

$$\gamma_{\Psi^0} = \sum_{i=1}^N |\phi_i\rangle\,\langle\phi_i|;$$

(3) The ground state energy and the ground state density operators are obtained by solving the minimization problem

$$\inf\Big\{E^0_{\rho^{\rm nuc}}(\gamma),\ \ \gamma \in \mathcal{S}(L^2(\mathbb{R}^3)),\ 0 \leqslant \gamma \leqslant 1,\ \mathrm{Tr}(\gamma) = N,\ \mathrm{Tr}(-\Delta\gamma) < \infty\Big\}. \tag{4.27}$$

The advantages of the density operator formulation, which are not obvious for finite systems (except for numerical purposes [22]), will clearly appear in Section 4.2.1.4, where we deal with crystals.

4.2.1.3 The Hartree model

Variational formulation.

Let us now reintroduce the Coulomb interaction between electrons, taking as a starting point the non-interacting system introduced in Section 4.1.1.2, reformulated in terms of density operators. There are several approximations of (4.4), which all share the same mathematical structure: their ground state energies and densities are obtained by minimizing some explicit functional $E_{\rho^{\rm nuc}}(\gamma)$ over the set of density operators $\mathcal{P}_N$. We focus in Sections 4.2.2 and 4.2.3 on the Hartree model

$$\inf\left\{E^{\rm Hartree}_{\rho^{\rm nuc}}(\gamma),\ \ \gamma\in\mathcal{S}(L^2(\mathbb{R}^3)),\ 0\leqslant\gamma\leqslant 1,\ {\rm Tr}(\gamma)=N,\ {\rm Tr}(-\Delta\gamma)<\infty\right\},\tag{4.28}$$

with

$$E^{\rm Hartree}_{\rho^{\rm nuc}}(\gamma)={\rm Tr}\left(-\frac{1}{2}\Delta\gamma\right)+\int_{\mathbb{R}^3}\rho_\gamma V^{\rm nuc}+\frac{1}{2}D(\rho_\gamma,\rho_\gamma),$$

where

$$D(f,g)=\int_{\mathbb{R}^3}\int_{\mathbb{R}^3}\frac{f(x)\,g(x')}{|x-x'|}\,dx\,dx'\tag{4.29}$$

is the classical Coulomb interaction. Note that $D(f,g)$ is well defined for example for f and g in $L^{6/5}(\mathbb{R}^3)$, see for instance [124, Section IX.4]. Recall also that for each $\gamma\in\mathcal{P}_N$, $\rho_\gamma\in L^1(\mathbb{R}^3)\cap L^3(\mathbb{R}^3)\hookrightarrow L^{6/5}(\mathbb{R}^3)$.

The existence of a minimizer to (4.28) for a neutral or positively charged system is established in [141]. The key-property allowing for a comprehensive mathematical analysis of the bulk limit for the Hartree model considered in Section 4.2.1.4 is that the ground state *density* is unique. This means that in the Hartree framework, all the minimizers to (4.28) share the same density. Such a uniqueness property of the ground-state density is not known to hold for other models of electronic structure, such as the Hartree-Fock model or Kohn-Sham models [99] of Density Functional Theory (DFT) [46, 86, 108].

Euler-Lagrange equations.

The Euler equation for the Hartree model reads

$$\left\{\begin{array}{l}\displaystyle\gamma^0=\sum_{i=1}^{+\infty}n_i|\phi_i\rangle\langle\phi_i|,\qquad \rho^0(x)=\rho_{\gamma^0}(x)=\sum_{i=1}^{+\infty}n_i|\phi_i(x)|^2,\\ H^0\phi_i=\varepsilon_i\phi_i,\qquad \langle\phi_i,\phi_j\rangle=\delta_{ij},\\ \displaystyle n_i=1\text{ if }\varepsilon_i<\varepsilon_{\rm F},\ 0\leqslant n_i\leqslant 1\text{ if }\varepsilon_i=\varepsilon_{\rm F},\ n_i=0\text{ if }\varepsilon_i>\varepsilon_{\rm F},\qquad \sum_{i=1}^{+\infty}n_i=N,\\ \displaystyle H^0=-\frac{1}{2}\Delta+V^0,\\ -\Delta V^0=4\pi(\rho^{\rm nuc}-\rho^0).\end{array}\right.\tag{4.30}$$

It can be proved that the essential spectrum of the self-adjoint operator H^0 is equal to $\mathbb{R}_+$ and that, for a neutral or positively charged system, H^0 has at least N negative eigenvalues. The scalar $\varepsilon_{\rm F}$, called the Fermi level, can be interpreted as the Lagrange multiplier of the constraint ${\rm Tr}(\gamma^0)=N$.

Assuming that $\varepsilon_N<\varepsilon_{N+1}$, the ground state density operator γ^0 of the Hartree model is unique: It is the orthogonal projector

$$\gamma^0=\sum_{i=1}^{N}|\phi_i\rangle\langle\phi_i|.$$

In this case, (4.30) can be rewritten under the more compact form

$$\begin{cases} \gamma^0 = 1_{(-\infty,\varepsilon_{\rm F}]}(H^0), \qquad \rho^0 = \rho_{\gamma^0}, \\ H^0 = -\dfrac{1}{2}\Delta + V^0, \\ -\Delta V^0 = 4\pi(\rho^{\rm nuc} - \rho^0), \end{cases} \tag{4.31}$$

for any $\varepsilon_{\rm F} \in (\varepsilon_N, \varepsilon_{N+1})$. In this equation, the notation $1_{(-\infty,\varepsilon_{\rm F}]}(H^0)$ is used for the spectral projector of H^0 corresponding to the spectrum in the interval $(-\infty, \varepsilon_{\rm F}]$.

Time-dependent model.

The time-dependent version of the Hartree model formally reads

$$\mathrm{i}\frac{d\gamma}{dt} = [H^0_\gamma, \gamma], \qquad H^0_\gamma = -\frac{1}{2}\Delta + V^{\rm nuc} + \rho_\gamma \star |\cdot|^{-1}, \tag{4.32}$$

where $[A, B] = AB - BA$ denotes the commutator of the operators A and B. When the system is subjected to some external time-dependent potential $v(t)$ (modeling for instance the displacement of some nuclei), the evolution is

$$\mathrm{i}\frac{d\gamma}{dt} = [H^v_\gamma, \gamma], \qquad H^v_\gamma = H^0_\gamma + v. \tag{4.33}$$

We do not give the precise mathematical meaning of the formal equations (4.32) or (4.33) for finite systems, but refer the reader to [5] and references therein (see in particular [39, Section XVII.B.5]) for further precisions. On the other hand, we will define and study a mild solution of such equations (see for instance [122] for a definition of this class of solutions) in the case of crystals with defects in Section 4.2.

The time-evolution corresponding to the Hartree model is known as the time-dependent self-consistent field equation, and is in fact equivalent under some assumptions to the so-called random phase approximation; see the discussion in [52].

Propagators are an important tool to study the evolution of systems described by time dependent Hamiltonians. Recall that a two-parameter family of unitary operators $U(t, s)$ $(s, t \in \mathbb{R})$ on $L^2(\mathbb{R}^3)$ is a unitary propagator provided (see [124, Section X.12]) (i) $\forall (r, s, t) \in \mathbb{R}^3, U(t, s)U(s, r) = U(t, r)$; (ii) $U(t, t) = 1$ (the identity operator); and (iii) $U(t, s)$ is jointly strongly continuous in t and s.

4.2.1.4 The Hartree model for crystals

The Hartree model presented in the previous section describes a *finite* system of N electrons in the electrostatic potential created by a nuclear density of charge $\rho^{\rm nuc}$. Crystals are, on the other hand, infinite periodic assemblies of nuclei surrounded by their electronic clouds. We consider therefore the bulk limit where the nuclear density of the perfect crystal is described by a $\mathcal{R}$-periodic distribution $\rho^{\rm nuc}_{\rm per}$, $\mathcal{R} = \mathbb{Z}a_1 + \mathbb{Z}a_2 + \mathbb{Z}a_3$ denoting a periodic lattice of $\mathbb{R}^3$ ((a_1, a_2, a_3) is a given triplet of linearly independent vectors of $\mathbb{R}^3$). A unit cell of $\mathcal{R}$ is denoted by Γ. Functional spaces of periodic functions are defined as

$$L^2_{\rm per}(\Gamma) = \left\{ u \in L^2_{\rm loc}(\mathbb{R}^3) \;\middle|\; u \ \mathcal{R}\text{-periodic} \right\},$$

and similar definitions hold for $H^k_{\rm per}(\Gamma)$, etc.

Bloch-Floquet transform

The Bloch-Floquet theory was introduced by Floquet for periodic differential equations and generalized by Bloch to periodic partial differential equations. We just recall the basic results we need and refer the reader to [125] for instance for further precisions.

The reciprocal lattice of the lattice $\mathcal{R}$ is $\mathcal{R}^* = \mathbb{Z}a_1^* + \mathbb{Z}a_2^* + \mathbb{Z}a_3^*$, with $a_i \cdot a_j^* = 2\pi\delta_{ij}$. We denote by Γ^* the first Brillouin zone (which is in particular a unit cell of $\mathcal{R}^*$). Any function $f \in L^2(\mathbb{R}^3)$ can be decomposed by the Bloch-Floquet transform as

$$f(x) = \fint_{\Gamma^*} f_q(x)\, \mathrm{e}^{\mathrm{i}q\cdot x} dq,$$

where $\fint_{\Gamma^*}$ is a notation for $|\Gamma^*|^{-1}\int_{\Gamma^*}$ and where the functions f_q are defined as

$$f_q(x) = \sum_{R\in\mathcal{R}} f(x+R)\, \mathrm{e}^{-\mathrm{i}q\cdot(x+R)} = \frac{(2\pi)^{3/2}}{|\Gamma|} \sum_{K\in\mathcal{R}^*} \widehat{f}(q+K)\, \mathrm{e}^{\mathrm{i}K\cdot x}. \tag{4.34}$$

For almost all $q \in \mathbb{R}^3$, $f_q \in L^2_{\mathrm{per}}(\Gamma)$. Besides, $f_{q+K}(x) = f_q(x)\mathrm{e}^{-\mathrm{i}K\cdot x}$ for all $K \in \mathcal{R}^*$ and almost all $q \in \mathbb{R}^3$. Lastly,

$$\|f\|^2_{L^2(\mathbb{R}^3)} = \fint_{\Gamma^*} \|f_q\|^2_{L^2_{\mathrm{per}}(\Gamma)}\, dq.$$

The main interest of the Bloch-Floquet transform (4.34) is that it provides a "block diagonalization" of any $\mathcal{R}$-periodic operator, that is of any operator on $L^2(\mathbb{R}^3)$ that commutes with translations operators τ_R for all $R \in \mathcal{R}$. Consider first a bounded $\mathcal{R}$-periodic operator A on $L^2(\mathbb{R}^3)$. Then there exists a family $(A_q)_{q\in\Gamma^*}$ of bounded operators on $L^2_{\mathrm{per}}(\Gamma)$ such that

$$\forall v \in L^2(\mathbb{R}^3), \quad (Av)_q = A_q v_q \quad \text{for almost all } q \in \Gamma^*. \tag{4.35}$$

If, in addition, A is self-adjoint on $L^2(\mathbb{R}^3)$, then A_q is self-adjoint on $L^2_{\mathrm{per}}(\Gamma)$ for almost all $q \in \Gamma^*$ and

$$\sigma(A) = \overline{\bigcup_{q\in\Gamma^*} \sigma(A_q)}.$$

Introducing the orthonormal Fourier basis $(e_K)_{K\in\mathcal{R}^*}$ of $L^2_{\mathrm{per}}(\Gamma)$, with $e_K(x) = |\Gamma|^{-1/2}\mathrm{e}^{\mathrm{i}K\cdot x}$, it follows from (4.35) that any bounded $\mathcal{R}$-periodic operator on $L^2(\mathbb{R}^3)$ is completely characterized by the Bloch-Floquet matrices

$$\Big(\big[A_{K,K'}(q)\big]_{(K,K')\in\mathcal{R}^*\times\mathcal{R}^*}\Big)_{q\in\Gamma^*}$$

defined for almost all $q \in \Gamma^*$ by $A_{K,K'}(q) = \langle e_K, A_q e_{K'}\rangle_{L^2_{\mathrm{per}}(\Gamma)}$. In particular, for all $(K, K') \in \mathcal{R}^* \times \mathcal{R}^*$ and almost all $q \in \Gamma^*$,

$$\forall v \in L^2(\mathbb{R}^3), \quad \mathcal{F}(Av)(q+K) = \sum_{K'\in\mathcal{R}^*} A_{K,K'}(q)\mathcal{F}v(q+K'). \tag{4.36}$$

For unbounded operators, the situation is slightly more intricate. Let us limit ourselves to the case of $\mathcal{R}$-periodic Schrödinger operators of the form

$$H = -\frac{1}{2}\Delta + V_{\mathrm{per}}$$

with $V_{\mathrm{per}} \in L^2_{\mathrm{per}}(\Gamma)$. By the Kato-Rellich theorem and [125, Theorem XIII.96], the operator H is self-adjoint on $L^2(\mathbb{R}^3)$, with domain $H^2(\mathbb{R}^3)$. It can also be decomposed as follows:

$$\forall v \in H^2(\mathbb{R}^3), \quad v_q \in H^2_{\mathrm{per}}(\Gamma) \quad \text{and} \quad (Hv)_q = H_q v_q \quad \text{for almost all } q \in \Gamma^*,$$

where H_q is the self-adjoint operator on $L^2_{\mathrm{per}}(\Gamma)$ with domain $H^2_{\mathrm{per}}(\Gamma)$, defined by

$$H_q = -\frac{1}{2}\Delta - iq \cdot \nabla + \frac{|q|^2}{2} + V_{\mathrm{per}}.$$

It is easily seen that for each $q \in \Gamma^*$, H_q is bounded below and has a compact resolvent. Consequently, there exists a sequence $(\varepsilon_{n,q})_{n\geq 1}$ of real numbers going to $+\infty$, and an orthonormal basis $(u_{n,q})_{n\geq 1}$ of $L^2_{\mathrm{per}}(\Gamma)$ such that

$$H_q = \sum_{n=1}^{+\infty} \varepsilon_{n,q} |u_{n,q}\rangle\langle u_{n,q}|.$$

As the mapping $q \mapsto H_q$ is polynomial on $\mathbb{R}^3$, it is possible to label the eigenvalues $\varepsilon_{n,q}$ in such a way that $(\varepsilon_{n,0})_{n\geq 1}$ is non-decreasing and that for each $n \geq 1$, the mapping $q \mapsto \varepsilon_{n,q}$ is analytic in each direction. Then, the spectrum is the union of bands

$$\sigma(H) = \overline{\bigcup_{q\in\Gamma^*} \sigma(H_q)} = \bigcup_{n\geq 1} \left[\Sigma_n^-, \Sigma_n^+\right],$$

with

$$\Sigma_n^- = \min_{q\in\overline{\Gamma^*}} \varepsilon_{n,q}, \quad \Sigma_n^+ = \max_{q\in\overline{\Gamma^*}} \varepsilon_{n,q}. \tag{4.37}$$

The interval $[\Sigma_n^-, \Sigma_n^+]$ is called the n^{th} band of the spectrum of H. It is possible to prove that the spectrum of H is purely absolutely continuous [145]. In particular, H has no eigenvalues.

Perfect crystals

The bulk limit argument allowing to obtain the correct limiting model to describe crystals in the Hartree framework has been rigorously founded by Catto, Le Bris and Lions in [28], for nuclei of unit charge on the cubic lattice $\mathbb{Z}^3$. It is also possible to justify the periodic Hartree model by passing to the limit on a supercell model with artificial periodic boundary conditions (see [23]). The latter approach is less physical, but technically much easier, and its extension to arbitrary crystalline structures is straightforward.

The model obtained by passing to the limit in (4.31) reads

$$\begin{cases} \gamma^0_{\mathrm{per}} = 1_{(-\infty,\varepsilon_{\mathrm{F}}]}(H^0_{\mathrm{per}}), \qquad \rho^0_{\mathrm{per}} = \rho_{\gamma^0_{\mathrm{per}}}, \\ H^0_{\mathrm{per}} = -\dfrac{1}{2}\Delta + V^0_{\mathrm{per}}, \\ -\Delta V^0_{\mathrm{per}} = 4\pi(\rho^{\mathrm{nuc}}_{\mathrm{per}} - \rho^0_{\mathrm{per}}), \end{cases} \tag{4.38}$$

with

$$\int_\Gamma \rho^0_{\mathrm{per}} = \int_\Gamma \rho^{\mathrm{nuc}}_{\mathrm{per}} = N \tag{4.39}$$

in order for the periodic Coulomb equation $-\Delta V^0_{\mathrm{per}} = 4\pi(\rho^{\mathrm{nuc}}_{\mathrm{per}} - \rho^0_{\mathrm{per}})$ to have a solution. As V^0_{per} is $\mathcal{R}$-periodic (and belongs to $L^2_{\mathrm{per}}(\Gamma)$ even for point-like nuclei), the operator H^0_{per} can be decomposed using the Bloch-Floquet transform:

$$\left(H^0_{\mathrm{per}}\right)_q = -\frac{1}{2}\Delta - iq \cdot \nabla + \frac{|q|^2}{2} + V^0_{\mathrm{per}} = \sum_{n=1}^{+\infty} \varepsilon_{n,q} |u_{n,q}\rangle\langle u_{n,q}|. \tag{4.40}$$

The operator $\gamma^0_{\mathrm{per}} = 1_{(-\infty,\varepsilon_{\mathrm{F}}]}(H^0_{\mathrm{per}})$ is a bounded self-adjoint operator which commutes with the translations $(\tau_R)_{R\in\mathcal{R}}$, and its Bloch-Floquet decomposition reads

$$\left(\gamma^0_{\rm per}\right)_q = \sum_{n=1}^{+\infty} 1_{\{\varepsilon_{n,q}\leqslant\varepsilon_{\rm F}\}} |u_{n,q}\rangle\langle u_{n,q}|.$$

Actually, the set $\{q \in \Gamma^* \,|\, \exists n \geq 1 \text{ s.t. } \varepsilon_{n,q} = \varepsilon_{\rm F}\}$ is of measure zero since the spectrum of $H^0_{\rm per}$ is purely continuous. It follows that $\gamma^0_{\rm per}$ is always an orthogonal projector, even if $\varepsilon_{\rm F}$ belongs to the spectrum of $H^0_{\rm per}$.

Using the Bloch decomposition of $\gamma^0_{\rm per}$, we can write the density $\rho^0_{\rm per}$ as

$$\rho^0_{\rm per}(x) = \fint_{\Gamma^*} \sum_{n=1}^{+\infty} 1_{\{\varepsilon_{n,q}\leqslant\varepsilon_{\rm F}\}} |u_{n,q}(x)|^2 \, dq.$$

Integrating on Γ, using (4.39) and the orthonormality of the functions $(u_{n,q})_{n\geq 1}$ in $L^2_{\rm per}(\Gamma)$, we obtain

$$N = \frac{1}{|\Gamma^*|} \sum_{n=1}^{+\infty} \left|\{q \in \Gamma^* \mid \varepsilon_{n,q} \leqslant \varepsilon_{\rm F}\}\right|. \tag{4.41}$$

This equation uniquely determines the value of the Fermi level $\varepsilon_{\rm F}$. It is easy to see that if the periodic Coulomb potential is shifted by a uniform constant C, and if $\varepsilon_{\rm F}$ is replaced with $\varepsilon_{\rm F} + C$, then $\gamma^0_{\rm per}$ and $\rho^0_{\rm per}$ remain unchanged.

The results from [23, 28] ensure that (4.38) is well-posed. In particular, the Hartree ground state density operator $\gamma^0_{\rm per}$ and the density $\rho^0_{\rm per}$ are uniquely defined. In addition, the periodic Coulomb potential $V^0_{\rm per}$ and the Fermi level $\varepsilon_{\rm F}$ are uniquely defined up to an additive constant, while $V^0_{\rm per} - \varepsilon_{\rm F}$ is uniquely defined. Besides, $\gamma^0_{\rm per}$ can be obtained by minimizing some periodic energy functional on the unit cell Γ.

In Sections 4.2.2 and 4.2.3, we assume that the system is an insulator (or a semi-conductor) in the sense that the $N^{\rm th}$ band is strictly below the $(N+1)^{\rm st}$ band:

$$\Sigma^+_N = \max_{q\in\Gamma^*} \varepsilon_{N,q} < \min_{q\in\Gamma^*} \varepsilon_{N+1,q} = \Sigma^-_{N+1}.$$

In this case, one can choose for $\varepsilon_{\rm F}$ any number in the range $(\Sigma^+_N, \Sigma^-_{N+1})$. For simplicity we set in the following

$$\varepsilon_{\rm F} = \frac{\Sigma^+_N + \Sigma^-_{N+1}}{2}$$

and denote by

$$g = \Sigma^-_{N+1} - \Sigma^+_N > 0 \tag{4.42}$$

the band gap.

4.2.1.5 The time-independent Hartree model for defects in crystals

Finally, we briefly recall the main properties of the time-independent model for crystals with a localized defect (see [23, 24] for a detailed analysis). The charge of the defect is denoted by ν, so that the total nuclear charge density is $\rho^{\rm nuc}_{\rm per} + \nu$. Conditions on ν are provided in (4.50) below. It is proved in [23] by means of bulk limit arguments that, for insulating and semiconducting materials, the ground state density matrix of a crystal reads

$$\gamma = \gamma^0_{\rm per} + Q_{\nu,\varepsilon_{\rm F}}. \tag{4.43}$$

The proof is performed for a nuclear charge $\rho^{\rm nuc}_{\rm per} \in L^2_{\rm loc}(\mathbb{R}^3)$, corresponding to smeared nuclei. However, as proved in [24], the limiting model describing the state of the defect (see (4.48) below) makes sense for point-like nuclei.

We first need to introduce the Coulomb space

$$\mathcal{C} := \left\{ f \in \mathscr{S}'(\mathbb{R}^3) \;\middle|\; \widehat{f} \in L^1_{\rm loc}(\mathbb{R}^3),\ |\cdot|^{-1}\widehat{f}(\cdot) \in L^2(\mathbb{R}^3) \right\},$$

where $\mathscr{S}'$ denotes the space of tempered distributions, the dual of the Schwartz space $\mathscr{S}$. Endowed with the scalar product extending (4.29) and defined by

$$D(f_1, f_2) := 4\pi \int_{\mathbb{R}^3} \frac{\overline{\widehat{f_1}(k)}\, \widehat{f_2}(k)}{|k|^2}\, dk,$$

the space $\mathcal{C}$ is a Hilbert space. Recall that $L^{6/5}(\mathbb{R}^3) \hookrightarrow \mathcal{C}$ and that, for f_1 and f_2 in $L^{6/5}(\mathbb{R}^3)$,

$$D(f_1, f_2) = \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{f_1(x)\, f_2(y)}{|x-y|} dx\, dy. \tag{4.44}$$

Considering $L^2(\mathbb{R}^3)$ as a pivot space, the dual space of $\mathcal{C}$ is

$$\mathcal{C}' := \left\{ V \in L^6(\mathbb{R}^3) \,|\, \nabla V \in (L^2(\mathbb{R}^3))^3 \right\},$$

endowed with the inner product

$$\langle V_1, V_2 \rangle_{\mathcal{C}'} := \frac{1}{4\pi}\int_{\mathbb{R}^3} \nabla V_1 \cdot \nabla V_2 = \frac{1}{4\pi}\int_{\mathbb{R}^3} |k|^2 \overline{\widehat{V}_1(k)}\, \widehat{V}_2(k)\, dk.$$

The appropriate functional space to describe local defects is the convex set

$$\mathcal{K} = \left\{ Q \in \mathcal{Q} \;\middle|\; -\gamma^0_{\rm per} \leqslant Q \leqslant 1 - \gamma^0_{\rm per} \right\}, \tag{4.45}$$

with

$$\begin{aligned} \mathcal{Q} = \big\{ Q \in \mathfrak{S}_2 \mid Q^* = Q,\ \ Q^{--} \in \mathfrak{S}_1,\ Q^{++} \in \mathfrak{S}_1, \\ |\nabla| Q \in \mathfrak{S}_2,\ |\nabla| Q^{--} |\nabla| \in \mathfrak{S}_1,\ |\nabla| Q^{++} |\nabla| \in \mathfrak{S}_1 \big\}, \end{aligned} \tag{4.46}$$

where $\mathfrak{S}_1$ and $\mathfrak{S}_2$ respectively denote the spaces of trace-class and Hilbert-Schmidt operators on $L^2(\mathbb{R}^3)$, $Q^{--} = \gamma^0_{\rm per} Q \gamma^0_{\rm per}$ and $Q^{++} = (1-\gamma^0_{\rm per}) Q (1-\gamma^0_{\rm per})$. Endowed with the norm defined by

$$\|Q\|_{\mathcal{Q}} = \|(1-\Delta)^{1/2} Q\|_{\mathfrak{S}_2} + \|(1-\Delta)^{1/2} Q^{--} (1-\Delta)^{1/2}\|_{\mathfrak{S}_1} + \|(1-\Delta)^{1/2} Q^{++} (1-\Delta)^{1/2}\|_{\mathfrak{S}_1},$$

the space $\mathcal{Q}$ is a Banach space. It is proved in [23] that although a generic operator $Q \in \mathcal{Q}$ is not trace-class, it is possible to define a generalized trace $\mathrm{Tr}_0(Q) = \mathrm{Tr}(Q^{++}) + \mathrm{Tr}(Q^{--})$ and a density $\rho_Q \in L^2(\mathbb{R}^3) \cap \mathcal{C}$. In addition, the mapping which to $Q \in \mathcal{Q}$ associates $\rho_Q \in L^2(\mathbb{R}^3) \cap \mathcal{C}$ is continuous (see [23, Proposition 1]): there exists $C_\rho > 0$ such that

$$\|\rho_Q\|_{L^2 \cap \mathcal{C}} \leqslant C_\rho \|Q\|_{\mathcal{Q}} \tag{4.47}$$

for any $Q \in \mathcal{Q}$. Note that if $Q \in \mathcal{K} \cap \mathfrak{S}_1$, then of course $\mathrm{Tr}_0(Q) = \mathrm{Tr}(Q)$, $\rho_Q \in L^1(\mathbb{R}^3)$ and $\mathrm{Tr}(Q) = \int_{\mathbb{R}^3} \rho_Q$.

The operator $Q_{\nu,\varepsilon_{\rm F}}$ is obtained by minimizing over $\mathcal{K}$ the energy functional

$$E_{\nu,\varepsilon_{\rm F}}(Q) = \mathrm{Tr}_0\left(H^0_{\rm per} Q\right) - \int_{\mathbb{R}^3} \rho_Q (\nu \star |\cdot|^{-1}) + \frac{1}{2} D(\rho_Q, \rho_Q), \tag{4.48}$$

where $\mathrm{Tr}_0\left(H^0_{\rm per} Q\right)$ is a notation for

$$\mathrm{Tr}_0\left(H^0_{\rm per} Q\right) = \mathrm{Tr}\left(\left|H^0_{\rm per} - \varepsilon_{\rm F}\right|^{1/2} \left(Q^{++} - Q^{--}\right) \left|H^0_{\rm per} - \varepsilon_{\rm F}\right|^{1/2} \right) + \varepsilon_{\rm F} \mathrm{Tr}_0(Q). \tag{4.49}$$

The energy functional $E_{\nu,\varepsilon_{\rm F}}$ is well-defined on $\mathcal{K}$ for all ν such that

$$(\nu \star |\cdot|^{-1}) \in L^2(\mathbb{R}^3) + \mathcal{C}'. \tag{4.50}$$

The first term of $E_{\nu,\varepsilon_{\rm F}}$ makes sense as it holds

$$c_1(1-\Delta) \leqslant |H^0_{\rm per} - \varepsilon_{\rm F}| \leqslant c_2(1-\Delta) \tag{4.51}$$

for some constants $0 < c_1 < c_2 < \infty$ (see [23, Lemma 1]). The last two terms of $E_{\nu,\varepsilon_{\rm F}}$ are also well defined since $\rho_Q \in L^2(\mathbb{R}^3) \cap \mathcal{C}$ for all $Q \in \mathcal{K}$.

4.2.2 Response to a given time-dependent effective potential

The state $\gamma^0_{\rm per}$ of a perfect crystal at equilibrium does not evolve in time. On the other hand, if originally the system is not at equilibrium and/or if some external perturbation is applied, the state of the system evolves in time. We describe in this section how the crystal responds to some local (in space) external perturbation. By local we mean here that the potential generated by the defects has some integrability properties, see (4.58) below. Recall also that our analysis is limited to insulating (or semiconducting) materials, *i.e.* (4.42) is assumed to hold.

More precisely, consider the case when the mean-field Hamiltonian $H^0_{\rm per} = -\frac{1}{2}\Delta + V^0_{\rm per}$ of the perfect crystal (defined in (4.38)) is perturbed by a time-dependent effective potential $v(t,x)$, so that the system is described by the time-dependent Hamiltonian

$$H_v(t) = H^0_{\rm per} + v(t,\cdot) = -\frac{1}{2}\Delta + V^0_{\rm per} + v(t,\cdot). \tag{4.52}$$

The dynamics is characterized by the unitary propagator $U_v(t,s)$ associated with the effective time-dependent Hamiltonian H_v (see Section 4.2.2.1 for conditions on v ensuring that the evolution operator is indeed well defined), and the state of the system at time t is described by the density operator

$$\gamma(t) = U_v(t,0)\gamma^0 U_v(t,0)^*, \tag{4.53}$$

where γ^0 is the state of the system at time $t = 0$. Similar considerations hold for mean-field models such as (4.38), although the situation is more complicated since both the periodic potential $V^0_{\rm per}$ and the perturbation v depend self-consistently on the state γ. This situation is dealt with in Section 4.2.3, using the results obtained in this section.

Considering $v(t)$ as a perturbation of the time-independent Hamiltonian $H^0_{\rm per}$, it is natural, as in the time-independent description of defects presented in Section 4.2.1.5 (see in particular the definition (4.43)), to introduce

$$Q(t) = \gamma(t) - \gamma^0_{\rm per}. \tag{4.54}$$

The first aim of this section is to prove that, if initially $Q(0) \in \mathcal{Q}$, the Banach space allowing to describe local defects in crystals, then $Q(t) \in \mathcal{Q}$ at all subsequent times (see Section 4.2.2.1). We then focus on the linear response of Q with respect to v. This allows to define the polarization operator, which gives the electronic response of the crystal as a function of the external effective perturbation (see Section 4.2.2.2). Finally, we show in Section 4.2.2.3 how the results of [24] on the static polarization of crystals (which is the response of the electronic density to a given, time-independent potential) can be recovered from the time-dependent setting in some adiabatic limit where the effective time-dependent perturbation varies very slowly in time.

4.2.2.1 Nonlinear response to an external perturbing potential

We first define the evolution operator U_v associated with the time-dependent Hamiltonian (4.52) and give some of its properties. When $v \in C^1(\mathbb{R}, L^\infty(\mathbb{R}^3))$, Theorem X.71 in [124] gives the

existence of a unitary propagator $(U_v(t,t_0))_{(t_0,t)\in\mathbb{R}\times\mathbb{R}}$ on $L^2(\mathbb{R}^3)$ such that for each $\psi\in H^2(\mathbb{R}^3)$, and each $t_0\in\mathbb{R}$, $t\mapsto\phi_{t_0}(t)=U_v(t,t_0)\psi$ is in $C^1(\mathbb{R},L^2(\mathbb{R}^3))\cap C^0(\mathbb{R},H^2(\mathbb{R}^3))$, and satisfies

$$\mathrm{i}\frac{d\phi_{t_0}(t)}{dt}(t)=H_v(t)\phi_{t_0}(t),\qquad \phi_{t_0}(t_0)=\psi.$$

Besides, denoting by $U_0(t)=\mathrm{e}^{-\mathrm{i}tH^0_{\mathrm{per}}}$ the unitary propagator associated with the time-independent Hamiltonian H^0_{per}, $(U_v(t,t_0))_{(t_0,t)\in\mathbb{R}\times\mathbb{R}}$ is the unique unitary propagator satisfying the Dyson equation

$$\forall(t_0,t)\in\mathbb{R}\times\mathbb{R},\quad U_v(t,t_0)=U_0(t-t_0)-\mathrm{i}\int_{t_0}^t U_0(t-s)v(s)U_v(s,t_0)\,ds. \tag{4.55}$$

Under the weaker assumption that

$$v\in L^1_{\mathrm{loc}}(\mathbb{R}_+,L^\infty(\mathbb{R}^3)), \tag{4.56}$$

it can be proved (see [H30, Lemma 1]) that there exists a unique unitary propagator solution to (4.55). By extension, we will call $(U_v(t,t_0))_{(t_0,t)\in\mathbb{R}\times\mathbb{R}}$ the unitary operator associated with the time-dependent Hamiltonian $H_v(t)$.

We now consider the evolution equation (4.53). This evolution automatically propagates forward in time the conditions $\gamma^0\in\mathcal{S}(L^2(\mathbb{R}^3))$ and $0\leqslant\gamma^0\leqslant 1$. Using (4.53)-(4.55) and the fact that γ^0_{per} is a steady state of the system in the absence of perturbation ($U_0(t)\gamma^0_{\mathrm{per}}U_0(t)^*=\gamma^0_{\mathrm{per}}$), a simple calculation shows that $Q(t)$ satisfies the integral equation

$$\forall t\in\mathbb{R}_+,\quad Q(t)=U_0(t)Q^0U_0(t)^*-\mathrm{i}\int_0^t U_0(t-s)[v(s),\gamma^0_{\mathrm{per}}+Q(s)]U_0(t-s)^*\,ds, \tag{4.57}$$

where $Q^0=\gamma^0-\gamma^0_{\mathrm{per}}$. It is easy to see that under the assumption (4.56) on the effective potential v, the above integral equation has a unique solution in $C^0(\mathbb{R}_+,\mathcal{S}(L^2(\mathbb{R}^3)))$.

We now focus on the interesting and important case when $v(t)$ is the effective potential generated by a local defect, that is when

$$v(t)=v_{\mathrm{c}}(\rho(t))=\rho(t)\star|\cdot|^{-1}. \tag{4.58}$$

In order for the time evolution to be well defined, we assume that the electronic density of the defect is sufficiently regular, namely $\rho\in L^1_{\mathrm{loc}}(\mathbb{R},L^2(\mathbb{R}^3)\cap\mathcal{C})$. The mapping v_{c} is an invertible bounded linear operator from $\mathcal{C}$ to $\mathcal{C}'$, and it also defines a bounded operator from $L^2(\mathbb{R}^3)\cap\mathcal{C}$ to $L^\infty(\mathbb{R}^3)$. Hence, if $\rho\in L^1_{\mathrm{loc}}(\mathbb{R},L^2(\mathbb{R}^3)\cap\mathcal{C})$, the potential v defined by (4.58) satisfies (4.56). The following proposition shows that, in this case, (4.57) can be considered not only as an integral equation on $\mathcal{S}(L^2(\mathbb{R}^3))$, but also as an integral equation on the functional space $\mathcal{Q}$.

Proposition 4.2. *Consider $Q^0\in\mathcal{Q}$, $\rho\in L^1_{\mathrm{loc}}(\mathbb{R}_+,L^2(\mathbb{R}^3)\cap\mathcal{C})$ and v the effective potential (4.58). Then, the integral equation (4.57) has a unique solution in $C^0(\mathbb{R}_+,\mathcal{Q})$, and for all $t\in\mathbb{R}_+$, $\mathrm{Tr}_0(Q(t))=\mathrm{Tr}_0(Q^0)$. In addition, if $Q^0\in\mathcal{K}$, then $Q(t)\in\mathcal{K}$ for all $t\in\mathbb{R}_+$.*

The Dyson expansion consists in writing (formally for the moment) the solution $Q(t)$ of (4.57) as the series

$$Q(t)=U_0(t)Q^0U_0(t)^*+\sum_{n=1}^{+\infty}Q_{n,v}(t), \tag{4.59}$$

where the operators $Q_{n,v}(t)$ are obtained by inserting (4.59) into (4.57) and equating the terms involving n occurrences of the potential v. In particular, the linear response is given by

$$Q_{1,v}(t)=-\mathrm{i}\int_0^t U_0(t-s)\left[v(s),\gamma^0_{\mathrm{per}}+U_0(s)Q^0U_0(s)^*\right]U_0(t-s)^*\,ds, \tag{4.60}$$

and the following recursion relation holds true:

$$\forall n \geq 2, \quad Q_{n,v}(t) = -\mathrm{i}\int_0^t U_0(t-s)\,[v(s), Q_{n-1,v}(s)]\,U_0(t-s)^*\,ds. \tag{4.61}$$

The main result of this section is the following proposition.

Proposition 4.3. *Consider $\rho \in L^1_{\mathrm{loc}}(\mathbb{R}_+, L^2(\mathbb{R}^3)\cap\mathcal{C})$ and v the effective potential (4.58). For each $n \geqslant 1$, the operator $Q_{n,v}$ defined by (4.60) for $n = 1$ and by (4.61) for $n \geq 2$ is in $C^0(\mathbb{R}_+, \mathcal{Q})$, and, for any $n \geqslant 1$, $\mathrm{Tr}_0(Q_{n,v}(t)) = 0$ for all $t \in \mathbb{R}_+$. Besides, there exist $\beta, C_{\mathrm{com},\mathcal{Q}} > 0$ such that*

$$\forall n \geq 1, \quad \forall t \in \mathbb{R}_+, \quad \|Q_{n,v}(t)\|_{\mathcal{Q}} \leqslant \beta\frac{1+\|Q^0\|_{\mathcal{Q}}}{n!}\left(\beta C_{\mathrm{com},\mathcal{Q}}\int_0^t \|\rho(s)\|_{L^2\cap\mathcal{C}}\,ds\right)^n \tag{4.62}$$

and the right-hand side of (4.59) converges in $\mathcal{Q}$, uniformly on any compact subset of $\mathbb{R}_+$, to the unique solution to (4.57)-(4.58) in $C^0(\mathbb{R}_+, \mathcal{Q})$.

4.2.2.2 Linear response and definition of the polarization

The aim of this section is to motivate, using rigorous mathematical arguments, the formulae (4.73) for the polarization matrix usually encountered in the physics literature, known as the Adler-Wiser formulae [1, 154]. These expressions are established for a modified linear response involving some damping. Proposition 4.6 gives a mathematical meaning to the polarization formulae when the damping vanishes.

Definition of the polarization

Since the polarization is defined as the linear response of the electronic density with respect to variations of the external potential (see (4.64) below), we focus on the linear response operator

$$Q_{1,v}(t) = -\mathrm{i}\int_0^t U_0(t-s)\left[v(s), \gamma^0_{\mathrm{per}} + U_0(s)Q^0U_0(s)^*\right]U_0(t-s)^*\,ds$$

defined in (4.60). We choose in the sequel $Q^0 = 0$. When the external perturbation $v(t)$ is compactly supported in time in some interval $[-t_0, t_0]$, we can view the perturbation process as a dynamics starting in the distant past from an equilibrium state described by $Q(t) = 0$ up to time $t = -t_0$, and perturbed only for times $t \geqslant -t_0$. Upon changing the the reference time from 0 to $-t_0$, the following integral equation is then obtained:

$$\forall t \in \mathbb{R}, \qquad Q_{1,v}(t) = -\mathrm{i}\int_{-\infty}^t U_0(t-s)\left[v(s), \gamma^0_{\mathrm{per}}\right]U_0(t-s)^*\,ds. \tag{4.63}$$

The interest of this formulation (compared to the original formulation (4.60)) is that it can be interpreted as some time convolution, which can then be rewritten in a simpler manner using Fourier transforms in time. Since $v \mapsto Q_{1,v}$ defines a continuous linear mapping from $L^1(\mathbb{R}, \mathcal{C}')$ to $C^0_{\mathrm{b}}(\mathbb{R}, \mathcal{Q})$, where $C^0_{\mathrm{b}}(\mathbb{R}, \mathcal{Q})$ denotes the space of the continuous bounded $\mathcal{Q}$-valued functions on $\mathbb{R}$, it is then possible, by density, to consider external perturbations $v \in L^1(\mathbb{R}, \mathcal{C}')$, and not only perturbations with compact supports in time. Alternatively, for a given perturbation $\widetilde{v}(t)$ defined only for positive times, it is possible to write the linear response (4.60) as (4.63) upon considering $v(t) = \widetilde{v}(t)\mathbf{1}_{t\geqslant 0}$.

Since $Q_{1,v}(t) \in \mathcal{Q}$ for all $t \in \mathbb{R}$, a density $\rho_{Q_{1,v}}(t) \in L^2(\mathbb{R}^3)\cap\mathcal{C}$ can be associated to this operator in view of [23, Proposition 1]. This defines the polarization operator, which is the bounded linear mapping

$$\begin{aligned} \chi_0 \ : \ L^1(\mathbb{R}, \mathcal{C}') &\to C^0_{\rm b}(\mathbb{R}, L^2(\mathbb{R}^3) \cap \mathcal{C}) \\ v &\mapsto \rho_{Q_{1,v}}. \end{aligned} \tag{4.64}$$

In fact, it is more convenient to work with the mapping $\mathscr{E} = v_{\rm c}^{1/2} \chi_0 v_{\rm c}^{1/2}$. As $v_{\rm c}^{1/2}$ is an invertible bounded linear operator from $L^2(\mathbb{R}^3)$ onto $\mathcal{C}'$, and from $\mathcal{C}$ onto $L^2(\mathbb{R}^3)$, and as $L^2(\mathbb{R}^3) \cap \mathcal{C}' = H^1(\mathbb{R}^3)$, $\mathscr{E}$ is a continuous linear operator from $L^1(\mathbb{R}, L^2(\mathbb{R}^3))$ to $C^0_{\rm b}(\mathbb{R}, H^1(\mathbb{R}^3))$:

$$\begin{aligned} \mathscr{E} \ : \ L^1(\mathbb{R}, L^2(\mathbb{R}^3)) &\to C^0_{\rm b}(\mathbb{R}, H^1(\mathbb{R}^3)) \\ f &\mapsto v_{\rm c}^{1/2} \left(\rho_{Q_{1, v_{\rm c}^{1/2}(f)}} \right). \end{aligned} \tag{4.65}$$

In order to state our results, we need to introduce additional Fourier transforms taking the time variable into account. The partial Fourier transform with respect to the time variable, denoted by $\mathcal{F}_t f$, has the following normalization:

$$\left(\mathcal{F}_t f\right)(\omega, x) = \int_{-\infty}^{+\infty} f(t, x)\, {\rm e}^{{\rm i}\omega t}\, dt. \tag{4.66}$$

The spatial Fourier transform (4.23) is denoted by $\mathcal{F}_x$ in the sequel in order to avoid confusions. The space-time Fourier transform is then $\mathcal{F}_{t,x} = \mathcal{F}_t \mathcal{F}_x = \mathcal{F}_x \mathcal{F}_t$.

Damped linear response

In order to study the properties of the linear response, it is convenient to first focus on the *damped* linear response defined, for $\eta > 0$, as

$$Q^\eta_{1,v}(t) = -{\rm i} \int_{-\infty}^{t} U_0(t-s) \left[v(s), \gamma^0_{\rm per} \right] U_0(t-s)^* {\rm e}^{-\eta(t-s)}\, ds. \tag{4.67}$$

We introduce the associated damped linear response operator

$$\begin{aligned} \mathscr{E}^\eta \ : \ L^1(\mathbb{R}, L^2(\mathbb{R}^3)) &\to C^0_{\rm b}(\mathbb{R}, H^1(\mathbb{R}^3)) \cap L^1(\mathbb{R}, H^1(\mathbb{R}^3)) \\ f &\mapsto v_{\rm c}^{1/2} \left(\rho_{Q^\eta_{1, v_{\rm c}^{1/2}(f)}} \right). \end{aligned} \tag{4.68}$$

As shown below (see Proposition 4.6), the operator $\mathscr{E}^\eta$ is indeed an approximation of the operator $\mathscr{E}$. The interest of the operator $\mathscr{E}^\eta$ is that it has better regularity properties than the plain linear response $\mathscr{E}$.

For a given $\eta > 0$, we consider a simple closed contour $\mathscr{C}_\eta$ in the complex plane, symmetric with respect to the real axis, enclosing $\sigma(H^0_{\rm per}) \cap (-\infty, \varepsilon_{\rm F}]$, containing no element of $\mathbb{R} \pm {\rm i}\eta$ (see Figure 4.2), and such that

$$\operatorname{dist}\Big(\mathscr{C}_\eta, \sigma\left(H^0_{\rm per}\right) \cap (-\infty, \varepsilon_{\rm F}] \Big) \geqslant \frac{\eta}{3}, \qquad \operatorname{dist}\Big(\mathscr{C}_\eta, \mathbb{R} + {\rm i}\eta \Big) \geqslant \frac{\eta}{3}. \tag{4.69}$$

We can then prove the following result.

Proposition 4.4. *The operator $\mathscr{E}^\eta$ is bounded on $L^2(\mathbb{R}, L^2(\mathbb{R}^3))$ and, for $f_1, f_2 \in L^2(\mathbb{R}, L^2(\mathbb{R}^3))$,*

$$\left\langle f_2, \mathscr{E}^\eta f_1 \right\rangle_{L^2(L^2)} = \int_{\mathbb{R}} \left\langle \mathcal{F}_t f_2(\omega), \mathscr{E}^\eta(\omega) \mathcal{F}_t f_1(\omega) \right\rangle_{L^2(\mathbb{R}^3)} d\omega, \tag{4.70}$$

where, for $h_1, h_2 \in L^2(\mathbb{R}^3)$,

$$\left\langle \mathscr{E}^\eta(\omega) h_1, h_2 \right\rangle_{L^2(\mathbb{R}^3)} = \frac{1}{\pi} {\rm Im} \left(\oint_{\mathscr{C}_\eta} {\rm Tr}_{L^2(\mathbb{R}^3)} \left[\frac{(\gamma^0_{\rm per})^\perp}{z - (H^0_{\rm per} + \omega + {\rm i}\eta)} \overline{v_{\rm c}^{1/2}(h_2)} \frac{(\gamma^0_{\rm per})}{z - H^0_{\rm per}} v_{\rm c}^{1/2}(h_1) \right] dz \right). \tag{4.71}$$

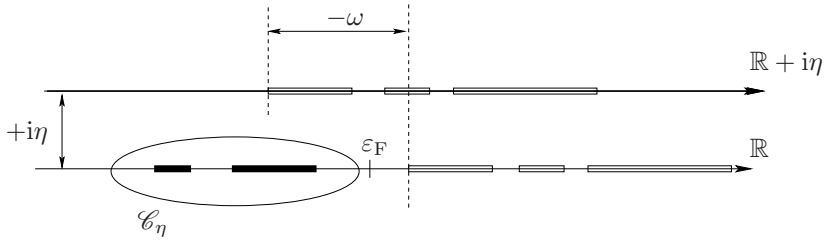


Fig. 4.2. Integration contour $\mathscr{C}_\eta$.

In addition, there exists a constant $C > 0$ such that

$$\|\mathscr{E}^\eta\|_{\mathcal{B}(L^2(\mathbb{R},L^2(\mathbb{R}^3)))} = \sup_{\omega\in\mathbb{R}} \|\mathscr{E}^\eta(\omega)\|_{\mathcal{B}(L^2(\mathbb{R}^3))} \leqslant \frac{C}{\eta^2}.$$

Since the linear response commutes with time translations, it is not surprising that the operator $\mathscr{E}^\eta$ is diagonal in the frequency domain (in the sense of (4.70)). Besides, the operators $\mathscr{E}^\eta(\omega)$ commute with spatial translations of the lattice. They are hence decomposed by the Bloch transform associated with the lattice $\mathcal{R}$. Equalities similar to (4.36) can be obtained. The action of $\mathscr{E}^\eta(\omega)$ on the fiber associated with the Bloch vector $q \in \Gamma^*$ is denoted by $\mathscr{E}^\eta(\omega, q)$. The Bloch matrices of the operator $\mathscr{E}^\eta(\omega)$ are then defined using the Fourier basis $(e_K)_{K\in\mathcal{R}^*}$ of $L^2_{\mathrm{per}}(\Gamma)$ as

$$\mathscr{E}^\eta_{K,K'}(\omega, q) = \langle e_K, \mathscr{E}^\eta(\omega, q) e_{K'} \rangle_{L^2_{\mathrm{per}}},$$

and it holds

$$\forall K \in \mathcal{R}^*, \quad \mathcal{F}_{t,x}\left(\mathscr{E}^\eta f\right)(\omega, q+K) = \sum_{K'\in\mathcal{R}^*} \mathscr{E}^\eta_{K,K'}(\omega, q)\, \mathcal{F}_{t,x} f(\omega, q+K'), \quad \text{for a.a. } (\omega, q) \in \mathbb{R}\times\Gamma^*. \tag{4.72}$$

As stated in the proposition below, the Bloch matrices of the operators $\mathscr{E}^\eta$ can be written in terms of the Bloch decomposition of the mean-field Hamiltonian H^0_{per}. As mentioned at the beginning of this section, the expressions (4.73) are known in the physics literature under the name of Adler-Wiser formulae [1, 154].

Proposition 4.5. *For each $\eta > 0$, the Bloch matrices of the damped linear response operator $\mathscr{E}^\eta$ are given by*

$$\mathscr{E}^\eta_{K,K'}(\omega, q) = \frac{\mathbf{1}_{\Gamma^*}(q)}{|\Gamma|} \frac{|q+K'|}{|q+K|} T^\eta_{K,K'}(\omega, q), \tag{4.73}$$

where the continuous functions $T^\eta_{K,K'} : \mathbb{R}\times\mathbb{R}^3 \to \mathbb{C}$ defined by

$$T^\eta_{K,K'}(\omega, q) = \sum_{n,m=1}^{+\infty} (\mathbf{1}_{n\leqslant N<m} - \mathbf{1}_{m\leqslant N<n}) \fint_{\Gamma^*} \frac{\langle u_{m,q'}, \mathrm{e}^{-\mathrm{i}K\cdot x}\, u_{n,q+q'}\rangle_{L^2_{\mathrm{per}}} \langle u_{n,q+q'}, \mathrm{e}^{\mathrm{i}K'\cdot x} u_{m,q'}\rangle_{L^2_{\mathrm{per}}}}{\varepsilon_{n,q+q'} - \varepsilon_{m,q'} - \omega - \mathrm{i}\eta}\, dq' \tag{4.74}$$

are uniformly bounded.

The above expressions are well defined (in particular, the sums are normally convergent).

Standard linear response

We now come back to the linear response defined in (4.65), which corresponds to the limit of the damped response (4.68) as $\eta \to 0$ (this limit is made precise in Proposition 4.6 below). It is not possible to pass to the limit directly in (4.73) since the denominators in (4.74) may vanish when $|\omega| > g$ (recall that g is the band gap of the host crystal, defined in (4.42)). The limit of the

expressions (4.73) is rather singular, and should be understood as a tempered distribution. It is therefore useful to first rewrite (4.72) using tempered distributions: for all $f \in \mathscr{S}(\mathbb{R}\times\mathbb{R}^3)$,

$$\mathcal{F}_{t,x}\left(\mathscr{E}^\eta f\right) = \sum_{K,K'\in\mathcal{R}^*} \tau_K\Big(\tau_{-K'}\left(\mathcal{F}_{t,x} f\right)\mathscr{E}^\eta_{K,K'}\Big), \tag{4.75}$$

where $\tau_K f(\omega,q) = f(\omega,q-K)$ is the momentum space translation of vector K. It can be proved that the series on the right hand side of (4.75) converges to $\mathcal{F}_{t,x}\left(\mathscr{E}^\eta f\right)$ in the sense of the tempered distributions. The Bloch-frequency decomposition of the operator $\mathscr{E}$ defined by (4.65) is then obtained by passing to the limit in (4.75) when $\eta\to 0$.

Proposition 4.6. *The operators $\mathscr{E}^\eta$ converge to $\mathscr{E}$ in the following sense: for any $f\in L^1(\mathbb{R},L^2(\mathbb{R}^3))$,*

$$\lim_{\eta\downarrow 0}\mathscr{E}^\eta f = \mathscr{E} f \quad \text{in } L^\infty_{\rm loc}(\mathbb{R},H^1(\mathbb{R}^3)).$$

Besides, for each $(K,K')\in\mathcal{R}^*\times\mathcal{R}^*$, the Bloch matrix $\mathscr{E}^\eta_{K,K'}$ converges in $\mathscr{S}'(\mathbb{R}\times\mathbb{R}^3)$, when η goes to zero, to a limiting distribution denoted by $\mathscr{E}_{K,K'}$. Finally, for each $f\in\mathscr{S}(\mathbb{R}\times\mathbb{R}^3)$, the following equality holds in $\mathscr{S}'(\mathbb{R}\times\mathbb{R}^3)$:

$$\mathcal{F}_{t,x}\left(\mathscr{E} f\right) = \sum_{K,K'\in\mathcal{R}^*} \tau_K\Big(\tau_{-K'}\left(\mathcal{F}_{t,x} f\right)\mathscr{E}_{K,K'}\Big). \tag{4.76}$$

This result shows that the matrix $(\mathscr{E}_{K,K'})_{K,K'}$ can be interpreted as the Bloch matrix of the operator $\mathscr{E}$.

4.2.2.3 Adiabatic limit: static linear response

The linear response of the electronic density for time-independent perturbations was studied in [24]. The aim of this section is to recover the static polarization operator from the time-dependent one in some adiabatic limit.

The time-independent polarizability operator defined in [24, Proposition 1] reads

$$\begin{aligned}\widetilde{\mathscr{E}}^{\rm static} \;:\; & L^2(\mathbb{R}^3)\to L^2(\mathbb{R}^3)\\ & h\mapsto v_{\rm c}^{1/2}\left(\rho_{Q^{\rm static}_{1,v_{\rm c}^{1/2}(h)}}\right),\end{aligned} \tag{4.77}$$

with, for $V\in\mathcal{C}'$,

$$Q^{\rm static}_{1,V} = \frac{1}{2{\rm i}\pi}\oint_{\mathscr{C}_0}(z-H^0_{\rm per})^{-1}V(z-H^0_{\rm per})^{-1}\,dz,$$

where $\mathscr{C}_0$ is a simple closed contour in the complex plane enclosing $\sigma(H^0_{\rm per})\cap(-\infty,\varepsilon_{\rm F}]$ and containing no element of $\sigma\left(H^0_{\rm per}\right)\cap[\varepsilon_{\rm F},+\infty)$. We deduce from the results in [24] that

$$\forall (K,K')\in\mathcal{R}^*\times\mathcal{R}^*,\quad \widetilde{\mathscr{E}}^{\rm static}_{K,K'}(q) = \mathscr{E}_{K,K'}(0,q)\quad \text{for a.a. } q\in\Gamma^*.$$

The time-independent polarizability operator is therefore the zero-frequency limit of the dynamical response, obtained by setting $\omega=0$ in (4.73) and passing to the limit $\eta\to 0$.

This observation leads us to study the adiabatic limit of the linear response, where, for some sufficiently small parameter $\alpha>0$, the evolution of the time-dependent potential v is slowed down by replacing $v(t)$ by $v(\alpha t)$, and the effect of the perturbation is considered on longer times t/α in order to obtain a non-trivial result. More precisely, given a time dependent perturbation $v(t)$, we introduce the linear response $\widetilde{Q}^\alpha_{1,v}(t) = Q_{1,v(\alpha\cdot)}(t/\alpha)$ (where $Q_{1,v}$ is defined in (4.63)):

$$\widetilde{Q}^{\alpha}_{1,v}(t) = -\mathrm{i}\int_{-\infty}^{t/\alpha} U_0\left(\frac{t}{\alpha}-s\right)\left[v(\alpha s),\gamma^0_{\mathrm{per}}\right]U_0\left(\frac{t}{\alpha}-s\right)^* ds.$$

Equivalently, this procedure may be seen as accelerating the free evolution generated by H^0_{per} and appropriately rescaling the result. Indeed, a change of variables shows that

$$\widetilde{Q}^{\alpha}_{1,v}(t) = -\frac{\mathrm{i}}{\alpha}\int_{-\infty}^{t} U_0\left(\frac{t-s}{\alpha}\right)\left[v(s),\gamma^0_{\mathrm{per}}\right]U_0\left(\frac{t-s}{\alpha}\right)^* ds.$$

For any $\alpha > 0$, we introduce the rescaled linear response operator

$$\begin{aligned}\widetilde{\mathscr{E}}^{\alpha} \ : \ L^1(\mathbb{R},L^2(\mathbb{R}^3)) &\to C^0_{\mathrm{b}}(\mathbb{R},H^1(\mathbb{R}^3))\\ f &\mapsto v_{\mathrm{c}}^{1/2}\left(\rho_{\widetilde{Q}^{\alpha}_{1,v_{\mathrm{c}}^{1/2}(f)}}\right).\end{aligned} \tag{4.78}$$

Proposition 4.7. *For any function $f \in \mathscr{S}(\mathbb{R}\times\mathbb{R}^3)$,*

$$\lim_{\alpha\downarrow 0}\widetilde{\mathscr{E}}^{\alpha} f = \widetilde{\mathscr{E}}^{0} f \quad \textit{in } \mathscr{S}'(\mathbb{R}\times\mathbb{R}^3),$$

where for all $t\in\mathbb{R}$, $\left(\widetilde{\mathscr{E}}^{0} f\right)(t) = \widetilde{\mathscr{E}}^{\mathrm{static}}(f(t))$.

This result means that, in the adiabatic limit we consider, the linear response at time t only depends on $v(t)$. There is no memory effect. Moreover, the linear response at time t is given by the time-independent (or static) polarization operator $\widetilde{\mathscr{E}}^{\mathrm{static}}$ studied in [24, Proposition 4].

4.2.3 The time-dependent Hartree model for defects in crystals

We consider in this section the evolution of the state of a crystal with defects when the system evolves according to a nonlinear evolution equation generalizing the evolution (4.33) for finite systems. Formally, we write, as in (4.54), the state of the system in the thermodynamic limit as $\gamma(t) = \gamma^0_{\mathrm{per}} + Q(t)$. The key point is to take into account the perturbations of the potential arising from the perturbation of the electronic density. Still denoting by $v(t)$ the applied external perturbation, this amounts to replacing the effective time dependent Hamiltonian (4.52) by

$$H^v_{\gamma}(t) = H^0_{\mathrm{per}} + v(t) + v_{\mathrm{c}}(\rho_{Q(t)}).$$

The equation governing the time evolution of the defect can then be motivated by a formal thermodynamic limit of the evolution equation (4.33) for finite systems, leading to the following nonlinear dynamics:

$$\mathrm{i}\frac{dQ(t)}{dt} = \left[H^0_{\mathrm{per}} + \rho_{Q(t)}\star|\cdot|^{-1} + v(t), \gamma^0_{\mathrm{per}} + Q(t)\right]. \tag{4.79}$$

The well-posedness of this dynamics is discussed in Section 4.2.3.1. In a second step, we obtain in Section 4.2.3.2 the expression of the macroscopic dielectric permittivity in terms of the microscopic description of the crystals through some homogenization limit.

4.2.3.1 Well-posedness of the dynamics

We consider mild solutions of the von Neumann equation (4.79), for an applied perturbation $v(t) = -v_{\mathrm{c}}(\nu(t))$, with a nuclear charge distribution of defects $\nu(t) \in L^2(\mathbb{R}^3)\cap\mathcal{C}$ for all t. The notion of mild solution is defined in [122] for instance. Since $[H^0_{\mathrm{per}},\gamma^0_{\mathrm{per}}] = 0$, the mild solutions satisfy the following nonlinear integral equation:

$$\forall t \in \mathbb{R}_+, \quad Q(t) = U_0(t)Q^0U_0(t)^* - \mathrm{i}\int_0^t U_0(t-s)\Big[v_{\mathrm{c}}(\rho_{Q(s)}-\nu(s)), \gamma^0_{\mathrm{per}}+Q(s)\Big]U_0(t-s)^*ds, \quad (4.80)$$

for a given initial condition $Q^0 \in \mathcal{K}$ (recall that $\mathcal{K}$ is defined in (4.45)). We can prove the following result.

Theorem 4.2. *Let $\nu \in L^1_{\mathrm{loc}}(\mathbb{R}_+, L^2(\mathbb{R}^3)) \cap W^{1,1}_{\mathrm{loc}}(\mathbb{R}_+, \mathcal{C})$. Then, for any $Q^0 \in \mathcal{K}$, the time-dependent Hartree equation (4.80) has a unique solution in $C^0(\mathbb{R}_+, \mathcal{Q})$. Besides, for all $t \geq 0$, $Q(t) \in \mathcal{K}$ and $\mathrm{Tr}_0(Q(t)) = \mathrm{Tr}_0(Q^0)$. Finally, if $\gamma^0_{\mathrm{per}} + Q^0$ is an orthogonal projector, then $\gamma^0_{\mathrm{per}} + Q(t)$ is also an orthogonal projector for all $t \geqslant 0$.*

The proof of local existence and uniqueness is classical and is based upon a Banach fixed point argument in a well-chosen ball of $\mathcal{Q}$. Once local-in-time existence and uniqueness is ensured, it is possible to extend the well-posedness of the dynamics to all times by proving that the $\mathcal{Q}$-norm of $Q(t)$ does not blow up in finite time. This can be completed by controlling the growth of $\|Q(t)\|_{\mathcal{Q}}$ by means of the energy functional $\mathcal{E} : \mathbb{R}_+ \times \mathcal{Q} \to \mathbb{R}$ defined by

$$\mathcal{E}(t, Q) = \mathrm{Tr}_0(H^0_{\mathrm{per}}Q) - D(\rho_Q, \nu(t)) + \frac{1}{2}D(\rho_Q, \rho_Q), \quad (4.81)$$

where $\mathrm{Tr}_0(H^0_{\mathrm{per}}Q)$ is defined in (4.49).

Under appropriate regularity assumptions on Q^0 and ν, the unique solution of (4.80) is a classical solution of (4.79) (see [H30, Proposition 12]).

4.2.3.2 Macroscopic dielectric permittivity

We motivate in this section the definition of the dielectric matrix starting from the nonlinear evolution equation (4.80). We start with formal computations, which, to be justified, would require estimates on the long time behavior of $Q(t)$. Unfortunately, we do not have such estimates, see the discussion after Proposition 4.8. For the same reasons as the ones presented before (4.63), we choose $Q^0 = 0$ in (4.80) and change the reference time from 0 to t_0, letting then t_0 go to $-\infty$, formally obtaining

$$Q(t) = -\mathrm{i}\int_{-\infty}^t U_0(t-s)\Big[v_{\mathrm{c}}(\rho_{Q(s)} - \nu(s)), \gamma^0_{\mathrm{per}} + Q(s)\Big]U_0(t-s)^*ds. \quad (4.82)$$

The above integral equation can be rewritten as

$$Q(t) = Q_{1,v_{\mathrm{c}}(\rho_Q-\nu)}(t) + \widetilde{Q}_{2,v_{\mathrm{c}}(\rho_Q-\nu)}(t), \quad (4.83)$$

where the linear operator $Q_{1,v}$ is defined in (4.60), and where the remainder $\widetilde{Q}_{2,v_{\mathrm{c}}(\rho_Q-\nu)}(t)$ collects the higher order terms. Equation (4.83) can be reformulated in terms of electronic densities as

$$\rho_Q(t) = \left[\mathcal{L}(\nu - \rho_Q)\right](t) + r_2(t), \quad (4.84)$$

where $\mathcal{L} = -\chi_0 v_{\mathrm{c}}$ and $r_2(t) = \rho_{\widetilde{Q}_{2,v_{\mathrm{c}}(\rho_Q-\nu)(t)}}$, or, equivalently,

$$\left[(1+\mathcal{L})(\nu - \rho_Q)\right](t) = \nu(t) - r_2(t). \quad (4.85)$$

This motivates the following result.

Proposition 4.8 (Properties of the operator $\mathcal{L}$). *For any $0 < \Omega < g$ (where g is the band gap of the host crystal), the operator $\mathcal{L}$ is a non-negative, bounded, self-adjoint operator on the Hilbert space*

$$\mathscr{H}_\Omega = \Big\{ \varrho \in L^2(\mathbb{R}, \mathcal{C}) \,\Big|\, \mathrm{supp}(\mathcal{F}_{t,x}\varrho) \subset [-\Omega, \Omega] \times \mathbb{R}^3 \Big\},$$

endowed with the scalar product

$$\langle \varrho_2, \varrho_1 \rangle_{L^2(\mathcal{C})} = \int_{\mathbb{R}} D\Big(\varrho_2(t,\cdot), \varrho_1(t,\cdot)\Big)\, dt = 4\pi \int_{-\Omega}^{\Omega} \int_{\mathbb{R}^3} \frac{\overline{\mathcal{F}_{t,x}\varrho_2(\omega,k)}\mathcal{F}_{t,x}\varrho_1(\omega,k)}{|k|^2}\, d\omega\, dk.$$

Hence, $1 + \mathcal{L}$, considered as an operator on $\mathscr{H}_\Omega$, is invertible.

This result cannot be used as such to study (4.85) since, even when ν belongs to $\mathscr{H}_\Omega$, the nonlinear response r_2 generally involves frequencies with absolute values larger than Ω. This can be seen from the relation (4.61). For instance, $Q_{2,v}$ is a convolution between the time evolution U_0 of the perfect crystal, and products such as $vQ_{1,v}$. Since the time Fourier transform of each of the element of the latter product has support in $(-\Omega, \Omega)$, the time Fourier transform of their product has support in $(-2\Omega, 2\Omega)$.

In order to rigorously obtain the macroscopic dielectric permittivity from (4.85), some spatial rescaling should be performed. In the time-independent case dealt with in [24], the equivalent of the nonlinear term r_2 turns out to become negligible under this spatial rescaling. In order to prove that the same phenomenon occurs in the time-dependent case, we would need estimates on the time growth of the nonlinear term $r_2(t)$. Controlling this term is probably difficult since very few is known about the long time limit of dynamics such as (4.82). Typical tools to this end are Strichartz-like estimates, which allow to establish appropriate decays in time and prove scattering results (see for instance [126, Section XI.13]). Such inequalities are easy to prove for the operator $-\Delta$ on $L^2(\mathbb{R}^3)$. To our knowledge, the only known dispersion inequality for periodic Schrödinger operators is restricted to the one-dimensional setting, see the recent work [34]. The proof is based on the stationary phase method, but several fine estimates rely explicitly on the fact that the system is one-dimensional. It is unclear whether such results can be extended to three-dimensional systems.

We will therefore limit ourselves to pass to the macroscopic limit on the following *linear* problem, which can be seen as a simplification of (4.84): $\Omega \in (0, g)$ and $\nu \in \mathcal{H}_\Omega$ being given, seek $\rho_\nu \in \mathcal{H}_\Omega$ such that

$$\forall t \in \mathbb{R}, \quad [(1 + \mathcal{L})(\nu - \rho_\nu)](t) = \nu(t). \tag{4.86}$$

In order to obtain some macroscopic property, we consider the regime where the perturbation is weak but spread out over a large region, using the same spatial rescaling as in [24]. For $\eta > 0$, introduce the rescaled charge of the external perturbation

$$\nu_\eta(t,x) = \eta^3 \nu(t, \eta x). \tag{4.87}$$

Note that the total charge of the defect is preserved since $\int_{\mathbb{R}^3} \nu_\eta(t,x)\, dx = \int_{\mathbb{R}^3} \nu(t,x)\, dx$ for all $\eta > 0$ and all $t \in \mathbb{R}$. We also define the rescaled potential generated by the total charge of the defect $\nu_\eta - \rho_{\nu_\eta}$ as

$$W_\nu^\eta(t,x) = \eta^{-1} v_{\mathrm{c}}(\nu_\eta - \rho_{\nu_\eta})\left(t, \eta^{-1} x\right). \tag{4.88}$$

The scaling of the potential is such that, in the absence of dielectric response ($\mathcal{L} = 0$), the potential effectively seen by the crystal is $W_\nu^\eta = v_{\mathrm{c}}(\nu)$. We are then able to prove the following result.

Proposition 4.9. *There exists a smooth mapping $\varepsilon_{\mathrm{M}}(\omega)$ for $\omega \in (-g, g)$, with values in the space of symmetric 3×3 matrices, satisfying $\varepsilon_{\mathrm{M}}(\omega) \geqslant 1$ for all $\omega \in (-g, g)$, and such that, for all $\nu \in \mathcal{H}_\Omega$ ($0 < \Omega < g$), the rescaled potential W_ν^η defined by* (4.86)-(4.88) *converges weakly in $\mathcal{H}_\Omega$ when η goes to 0, to the unique solution W_ν in $\mathcal{H}_\Omega$ to the equation*

$$-\mathrm{div}\Big(\varepsilon_{\mathrm{M}}(\omega)\nabla\left[\mathcal{F}_t W_\nu\right](\omega,\cdot)\Big) = 4\pi\left[\mathcal{F}_t \nu\right](\omega,\cdot), \tag{4.89}$$

where div *and* ∇ *are the usual divergence and gradient operators with respect to the space variable* x*.*

A precise expression of $\varepsilon_{\mathrm{M}}(\omega)$ in terms of the Bloch decomposition of the mean-field Hamiltonian H^0_{per} is given in [H30]. Note that in the macroscopic equation (4.89), the pulsation ω enters only as a parameter: there is no coupling between different values of ω. In the space-time domain, this means that the charge $\nu(t,x)$ and the potential $W_\nu(t,x)$ are related by a space-time convolution.

Part III

Perspectives

5

Future directions

I present in this chapter some of the research tracks I intend to explore in the near future: numerical methods for nonequilibrium systems in statistical physics (Section 5.1), and mathematical and numerical analysis of models from quantum physics (Section 5.2).

5.1 Numerical methods for nonequilibrium systems in statistical physics

The computation of average properties of nonequilibrium systems, such as average values of the response functions considered in Section 3.1.3, is almost always performed using longtime averages over the nonequilibrium dynamics. In many situations however, these averages are not converging very fast because of the large variance of the estimator compared to the average value to be computed (see for instance the discussion in [H22]). Moreover, in some situations such as thermal transport computations in very long atom chains, long transient regimes have to be removed from the computation of the average. With my implementation of the numerical algorithms and the computers we have at CERMICS, this means sometimes discarding several weeks, if not months, of computations for the longest chains ($N \sim 100,000$). There is clearly a need for more efficient numerical techniques to compute linear response properties, and properties of nonequilibrium systems in general.

5.1.1 Variance reduction techniques

Variance reduction techniques are used on a daily basis in equilibrium simulations. The use of such techniques is often based on the explicit expression of the invariant measure, and its modification under appropriate perturbations. I have three strategies in mind: importance sampling, stratification, and the control variate method. As I argue below, none of these methods can be used as such for nonequilibrium systems. Indeed, the control variate method is an interesting technique for

very specific dynamics only; while the unpleasant behavior of the invariant measure of nonequilibrium systems under perturbations (described below) somehow prevents the use of importance sampling and stratification by constrained dynamics. This is of course related to the fact that nonequilibrium systems are really characterized by their dynamics, and the invariant measure is not as central a concept as for equilibrium systems.

5.1.1.1 Importance sampling

Importance sampling in computational statistical physics is implemented in practice in equilibrium methods by adding some biasing potential A to the Langevin dynamics or the Metropolis algorithm. The correctness of the procedure is based upon the fact that the perturbed measure is the original measure $Z^{-1}\mathrm{e}^{-\beta V}$ multiplied by a factor proportional to e^{A}, so that the microscopic configurations sampled by the biased dynamics can be reweighted in order to be distributed according to the measure of interest. There are several ways to find appropriate biasing potentials, using for instance the free energy associated with a slow degree of freedom (see the discussion in Section 2.2.1.3).

On the other hand, consider a nonequilibrium dynamics

$$dq_t = b(q_t)\,dt + \sigma dW_t,$$

with invariant measure $\psi_\infty(q)\,dq$, perturbed by a gradient term, such as

$$dq_t = \Big(b(q_t) + \nabla A(q_t)\Big)dt + \sigma dW_t.$$

We denote by $\psi_\infty^A(q)\,dq$ the invariant measure of this process (assuming that it exists). In general, $\psi_\infty^A(q)\,dq$ is different from $Z^{-1}\psi_\infty(q)\mathrm{e}^{A(q)}\,dq$ (consider for instance the simple example discussed after (3.5)). The expression of ψ_∞^A is actually not known, and has in general no simple relationship with the expression of ψ_∞. It is therefore unclear how to use importance sampling strategies for nonequilibrium systems.

5.1.1.2 Stratification

Stratification is another way of decomposing a difficult sampling problem in several easier ones. Typically, it can be applied by constraining the dynamics on the iso-surface of some slowly evolving degree of freedom, and varying the values of the constraint in order to sample the full phase-space, as is done in thermodynamic integration (see Section 2.2.2). For equilibrium systems, it is easy to construct constrained dynamics sampling the restriction of the invariant measure of the unconstrained dynamics.

The invariant measure of constrained nonequilibrium dynamics may, on the other hand, have no relationship whatsoever with the invariant measure of the unconstrained nonequilibrium dynamics. Let us illustrate this point by a simple example. Consider the dynamics

$$\begin{cases} dx_t^1 = \partial_{x_2} H(x_t^1, x_t^2) + \sqrt{2}\,dW_t^1, \\ dx_t^2 = -\partial_{x_1} H(x_t^1, x_t^2) + \sqrt{2}\,dW_t^2, \end{cases}$$

on the state space $\mathbb{T}^2$, for a given smooth periodic function H. A simple computation shows that $\psi_\infty = \mathbf{1}_{\mathbb{T}^2}$ is an invariant probability measure. Besides, this is the unique invariant probability measure since the process is ergodic. Consider now the constraint $\xi(x) = x_2$. The restriction of ψ_∞ to the space $\{x \in \mathbb{T}^2 \,|\, \xi(x) = 0\} = \mathbb{T} \times \{0\}$ is $\overline{\psi}_\infty(x_1) = \mathbf{1}_{\mathbb{T}}$. The process constrained using a constraining force in the direction of $\nabla\xi$ reads

$$dx_t^1 = f(x_t^1)\,dt + \sqrt{2}\,dW_t^1, \qquad f(x^1) = \partial_{x_2} H(x^1, 0).$$

In general, the invariant measure for this process is different from $\mathbf{1}_{\mathbb{T}}$. Indeed, introduce

$$F = \int_0^1 f, \qquad V(x^1) = \int_0^{x^1} (f(s) - F)\, ds.$$

Note that V is a periodic function ($V(0) = V(1) = 0$). The computations made in Section 3.1.1 show that the unique invariant measure of the constrained process is

$$\psi_\infty(x^1) = Z^{-1} \int_0^1 \mathrm{e}^{V(x^1+y)-V(x^1)-Fy}\, dy,$$

which is different from $\mathbf{1}_{\mathbb{T}}$ in general.

5.1.1.3 Control variate method

As far as I know, the only variance reduction technique I have seen applied to nonequilibrium systems is the control variate method, in the case of a fully stochastic dynamics [66], where the average flux of particles across the system is measured. The general idea of the control variate method for nonequilibrium systems is to simulate a system at equilibrium and a system subjected to a small external forcing, and to monitor the difference between the flux of interest in the nonequilibrium system, and the flux in the equilibrium one (which, up to statistical errors, should vanish). When the coupling is sufficiently strong, the variance of the difference of the fluxes is much smaller than the variance of the flux of the nonequilibrium system alone. On the other hand, this approach is useless in systems where the bulk dynamics is Hamiltonian since the coupling is too weak. An interesting question is then: Is there a way to modify the dynamics in order to increase its coupling properties, while keeping an appropriate linear response?

5.1.2 Variance reduction for nonequilibrium systems: some possible tracks

Finding general variance reduction techniques for nonequilibrium systems is a very challenging problem. A more amenable path is to understand the standard variance reduction techniques used for equilibrium systems in the linear response regime, benefiting from the expression of the invariant measure as a series expansion in powers of the magnitude of the forcing (see (3.17)).

5.1.2.1 Constraining nonequilibrium systems (stratification)

What does it mean to constrain nonequilibrium systems? Or, in a less schematic way, how should the constraining be performed, and what is the measure sampled by the constrained process? I have two motivations in mind:

(i) the computation of free energy differences. In this case, the constraint fixes the value of the reaction coordinate ξ, and the aim is to compute the normalization factor for the restriction of ψ_∞ to $\Sigma = \xi^{-1}\{0\}$. To this end, the constrained dynamics should sample the marginal of the invariant measure of the unconstrained dynamics. I expect that the appropriate constraining process to fulfill this requirement involves the (unknown) invariant measure, but the hope is that this dependence can be made explicit in the linear response regime, at least at first order;

(ii) the computation of transport properties of systems with molecular constraints, such as the computation of the shear viscosity by bulk-driven steady-state nonequilibrium methods for rigid models of water. The question is in this case: How should the constraints be implemented in order to have a consistent linear response theory, in the sense that the constraining process and the linear response procedure commute?

5.1.2.2 Non-physical dynamics

Another path to more efficient simulations is to more systematically explore the use of "non-physical" dynamics, that may have better convergence properties than standard dynamics.

(i) As described in Section 3.1.3, there are (infinitely) many equivalent ways of obtaining the correct linear response by choosing appropriately the perturbation applied to the system. This does not mean however that the corresponding numerical approaches are equivalent. In particular, the convergence to the steady state may be faster for some dynamics. The latter question may be reformulated mathematically by saying that we are looking for a perturbation $\mathcal{A}_1$ maximizing the spectral gap of the generator of the nonequilibrium dynamics $\mathcal{A}_0 + \xi\mathcal{A}_1$, under the constraint that the conjugated response $\xi\mathcal{A}_1^*\mathbf{1}$ is fixed.
It would be interesting for instance to compare the numerical performances of the three dynamics presented in Section 3.1.3.5 to begin with.

(ii) A possibly interesting approach is the simulation of systems with fixed fluxes, called Norton ensembles (see [55, Chapter 6] and [135]). In standard nonequilibrium dynamics, a forcing is applied to the reference dynamics (for instance, a temperature difference for thermal transport) and the average of some response function R (such as the energy current) is monitored. It may however be possible as well to fix exactly the value of the response function by appropriately constraining the system, and determine the forcing induced on the system. Linear response properties would then be obtained by dividing the fixed value of the response by the average forcing. I would like to understand how such a procedure works, and under which assumptions it is indeed consistent with the standard approach; and then compare its convergence properties (theoretically and/or numerically) with the convergence properties of the standard approaches.

5.2 Mathematical and numerical analysis of models in quantum physics

There are several problems which I would like to study in quantum physics, at the intersection of theoretical mathematical physics and numerical analysis.

First, many extensions of the work on the time dependent linear response of crystals presented in Section 4.2 can be envisioned:

- The linear response of the system can be studied in the case when the perturbation is not local, but is rather a global (weak) electromagnetic field.
  There are several models to describe magnetism in finite (molecular) systems. Let us present for instance the Hartree-Fock model for finite systems. It is fundamental to take the spin variable into account. The state of the system is therefore described by a density operator $\gamma \in \mathcal{S}(L^2(\mathbb{R}^2, \mathbb{C}^2))$, such that $0 \leqslant \gamma \leqslant 1$ and $\mathrm{Tr}(\gamma) = N$, with kernel

$$\gamma(x,y) = \begin{pmatrix} \gamma_{\uparrow\uparrow}(x,y) & \gamma_{\uparrow\downarrow}(x,y) \\ \gamma_{\downarrow\uparrow}(x,y) & \gamma_{\downarrow\downarrow}(x,y) \end{pmatrix}.$$

  The electronic density is $\rho_\gamma(x) = \mathrm{Tr}_{\mathbb{C}^2}(\gamma(x,x)) = \gamma_{\uparrow\uparrow}(x,x) + \gamma_{\downarrow\downarrow}(x,x)$, and the magnetization is the vector

$$m_\gamma(x) = (m_{\gamma,x_1}(x), m_{\gamma,x_2}(x), m_{\gamma,x_3}(x)), \qquad m_{\gamma,x_i}(x) = \mathrm{Tr}_{\mathbb{C}^2}\left(\sigma_i \gamma(x,x)\right),$$

  where $\sigma_1, \sigma_2, \sigma_3$ are the Pauli matrices. The energy of such a state in the Hartree-Fock model reads

$$E(\gamma) = \frac{1}{2}\mathrm{Tr}\Big((-\mathrm{i}\nabla + A_{\mathrm{ext}})^2\gamma\Big) + \int_{\mathbb{R}^3} V^{\mathrm{nuc}}\rho_\gamma + \int_{\mathbb{R}^3} m_\gamma \cdot B_{\mathrm{ext}} + \frac{1}{2}D(\rho_\gamma, \rho_\gamma)$$
$$- \frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{\sum_{\sigma,\sigma'\in\{\uparrow,\downarrow\}} |\gamma_{\sigma\sigma'}(x,y)|^2}{|x-y|}\,dx\,dy,$$

where B_{ext} is an external magnetic field, and A_{ext} is the associated potential vector. Other first principle models of electronic structure, such as spin density functional theory or current density functional theory and their extensions (see [53] and references therein), have forms similar to the Hartree-Fock energy.

At the macroscopic level, magnetism is described by Maxwell's equations. For crystals (infinite systems obtained in the thermodynamic limit), a fundamental issue would be to obtain an expression of the magnetic permeability from a homogenization limit of a quantum model describing magnetic crystals. I expect the mathematical techniques involved in this derivation to be similar enough to the ones used in Section 4.2. A first question is however to write an appropriate model describing magnetic crystals depending on the type of magnetism of interest (orbital *vs.* spin magnetism). For the free electron gas and tight-binding models, there are some recent results on the definition of the magnetic susceptibility for orbital magnetism [21, 137]. For nonlinear models of density functional theory, this is not the case. In fact, the spectral theory of effective, periodic magnetic Hamiltonians is still an active research topic [69, 98].

- Another interesting issue is the interaction of the electronic defects and the nuclear degrees of freedom. Vibrations of the nuclei around their equilibrium positions are described by phonons, which represent the elementary displacement waves of the underlying crystal lattice. Interactions between electronic states and phonons are modeled in the physical literature by appropriate (linear) couplings. I would like to investigate how such empirical couplings can be derived rigorously in some limiting regime from an underlying reference fully ab-initio model. This involves incorporating nuclear degrees of freedom in the model of electronic defects presented in [23, 24]. One mathematical difficulty will be that the perturbations of the nuclear lattice, arising from the relaxation of the nuclear degrees of freedom, are not necessary local.

There are also other models that are very relevant in applications, and which have not been investigated from a mathematical viewpoint:

- A first one is the GW method to compute electronic excitations such as the ones created by the incident light on photovoltaic cells [8, 58, 84, 85]. The unknown in this method is the Green's function of the system, which satisfies a self-consistent equation for a non-self adjoint Hamiltonian. The non-self adjointness arises from a frequency dependent exchange correlation term, which generalizes the standard functionals used in density functional theory (such as LDA or GGA). Formulating this model in an appropriate functional framework is already quite challenging.
- I would like also to investigate models for transport at the quantum level, in particular self-consistent models in the framework of nonequilibrium Green's functions (see [38] for a simple introduction to such techniques). For instance, it is not clear whether these nonlinear models are well posed (existence and uniqueness of a solution).

The mathematical difficulties common to all the models hinted at above are the nonlinearity of the equations and their genuine time-dependence.

Part IV

References

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